The Determination of Trace Impurities in Nickel Plating Baths.

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THE DETERMINATION OF TRACE IMPURITIES IN NICKEL PLATING BATHS

by

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The William H. Chandler Chemical Laboratory
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June, 1948

This dissertation is respectfully submitted to the Graduate Faculty of Lehigh University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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This dissertation is approved and accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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Analytical Methods:

Introduction

In previous years, commercial electroplaters tested their plating baths for only major constituents and if the concentration of these substances was satisfactory, the bath was in good condition. However, research later showed that the presence of small amounts of other elements in the bath could greatly affect the plating efficiency and the physical properties of the metal being plated. Thus, the presence of small quantities of lead in copper baths has been found to cause rough, dark colored deposits to which nickel deposits will not adhere. Also, the presence of small amounts of hexavalent chromium markedly decreases the plating efficiency of nickel baths and produce a deposit that peels off easily. These are only two examples of the serious effect the presence of impurities in a bath may have upon the success of plating operations.

Impurities find their way into plating baths from various sources. Commercial nickel salts used in preparing baths have been known to contain excessive amounts of lead and iron. Another main source is the water used in preparing the bath and replacing the water lost by evaporation. The soluble mineral constituents usually brought into the solution with water are iron, aluminum, calcium, manganese, sodium, potassium, and silicon. Other sources of bath contamination are the attack of the solutions on the metal of unlimed tanks; the dropping of particles to be plated into the bath and allowed to stay there; the presence of impurities in the anodes; the presence of accessory equipment such as piping, broken thermometer bulbs, immersion heaters in the bath; and many other miscellaneous causes.

The presence of these impurities in plating baths and their adverse effect upon plating operations call for means of determining their concentration and for methods of removing them from the bath before they cause trouble. Unfortunately, there have not been available analytical methods for the determination of these trace impurities in plating baths that could be run rapidly by non-skilled personnel. It is for the purpose of developing such methods that this work was initiated.

Methods of Separating Traces of Impurities

Commercial nickel plating baths usually contain nickel sulfate, nickel chloride and boric acid in varying amounts. Some are adjusted to a pH of about 3 to 4 and others are more highly acidic. On the average, there is about 90 grams of nickel per liter of bath. Hence, the first problem met in analyzing for traces of impurities in nickel baths is the separation of very small amounts of impurities from very large amounts of nickel. It would be ideal to find methods of analysis that would involve no separations but this proved to be the case for only one constituent--manganese.

At this point, it might not be amiss to review the customary methods used in separating the various components of a mixture of soluble compounds.

1) Precipitation Methods

In general, the precipitation of microgram quantities of a given constituent is difficult to carry out quantitatively. Many precipitations considered complete when working with 20-30 milligrams of material are not complete if only about 20-30 micrograms are present. For example, 100 milligrams of lead can be precipitated by 2-mercaptobenzothiazole with less than 0.1 milligram of lead remaining in solution--a quantity so small that the precipitation of lead with the reagent can be considered quantitative. However, if less than 0.1 milligrams of lead are to be precipitated, the separation will probably not be complete since quantities of this order of magnitude remain in solution when larger quantities of lead are precipitated. This point must always be considered when planning to precipitate microgram quantities of any constituent.

It has been shown that the addition of sizeable amounts of another ion which will precipitate with the same reagent used to precipitate the desired constituent will act as a "collector" and result in the quantitative recovery of the latter even when present in microgram quantities. Thus, in attempting to precipitate 10 micrograms of iron from a nickel bath with cupferron, the results were unsatisfactory. Later, experiments showed that if some copper was present, the iron could be quantitatively separated from the nickel with cupferron. The copper cupferride formed acts as a collector for the minute amount of iron cupferride present. While this technique can often result in the quantitative separation of micro quantities of a substance, the latter usually has to be separated from the collector material which detracts from the value of this method.

Separation of micro quantities of any constituent from a macro constituent by precipitating the latter does not ordinarily give satisfactory results because appreciable quantities of the constituent present in minute amounts are partially absorbed by the precipitate or the filter paper.

2) Electrolytic Methods

It is well known that microgram quantities of metallic ions can be quantitatively deposited from aqueous solutions and hence, electrodeposition can serve as a means of separating and in some case determining a desired element. Lead, copper, silver, and numerous other elements present in very small amounts have been determined in this way. However, attempts to apply this separation method to traces of impurities in plating baths is not too feasible. With a number of different impurities present, there is danger of plating several ions out simultaneously and making subsequent separations necessary. In addition, the electrodeposition of any ion from a bath full of nickel and other impurities is not likely to give a good, clean separation. One attempt was made to utilize this technique but with little success and hence it was not considered further.

3) Volatilization Methods

In such methods a volatile compound of the desired constituent is formed and then distilled and collected. For example, arsenic can be converted to the chloride and distilled from an aqueous solution containing a high concentration of hydrochloric acid. Tin can be separated from a mixture in which it is present in the stannic valence state by adding ammonium iodide to the mixture and heating. The tin forms volatile stannic iodide which is condensed and collected. The method serves admirably for the separation and determination of ammonia in the Kjeldahl method, but its value for the separation of metallic impurities is doubtful as long as other means can be found. In the first place, a reagent must be found which will form a volatile compound with the element one wants to separate from the solution. Secondly, special apparatus has to be assembled to distil, condense and collect the volatile compound. So while it might be possible to work out separations involving volatilization of a desired impurity in a plating bath, it cannot be done simply and without the utilization of fairly elaborate equipment.

4) Extraction Methods

Such methods involve the formation of a compound of the constituent sought that is more soluble in a solvent which is immiscible with water than it is in an aqueous phase. Then by successive extractions with the immiscible solvent, quantitative separations can be obtained. The quantity of any substance removed per extraction is a function of the volume of solvent, the volume of the aqueous phase and the relative solubility of the compound in the two liquids. This can be expressed by the formula

$$\frac{C}{C_1} = K \quad \ldots\ldots\ldots\ldots\ldots \quad (1)$$

where C = concentration of the solute per unit volume in solvent C, C_1 = the concentration of the solute per unit volume in solvent C_1 and K is called the distribution coefficient. It is constant for any given solute and the same two solvents. Once this constant is known, it is easy to calculate the concentration of the solute remaining in one phase and after any given number of extractions with a non-miscible solvent by use of the formula

$$X_n = x \quad \frac{W}{KL + W}^{\,n} \quad \ldots\ldots\ldots\ldots \quad (2)$$

where W = volume of solution containing x grams of solute
L = volume of the portions of the non-miscible solvent used
n = number of extractions made with the non-miscible solvent
X_n = number of grams of solute remaining in the first-solvent after (n) extractions
K = Distribution constant

Since many metals form complex ions that are soluble in organic solvents which are non-miscible with water, this extraction technique seemed to offer the greatest probability of successfully separating trace quantities of impurities from nickel plating baths. No elaborate apparatus is required, no filtering with dangers of co-precipitation or absorption of other ions are involved, the method is rapid. In addition the separated ion is still in solution and is easier to handle in subsequent steps than a precipitate which has to be redissolved. Hence, in developing analytical methods for trace constituents in nickel plating baths, emphasis was placed on the employment of extraction methods for separating these traces prior to the final determination of their concentration.

Examples of Extraction Separations Used in the Procedures Developed

Before briefly discussing the quantitative procedures worked out, it might be of some interest to illustrate in what different ways extraction separations were employed in the methods to be described later.

In the determination of iron, advantage was taken of the fact that cupferron will precipitate small quantities of iron without forming insoluble nickel cupferrides in acid solutions. It was noted that the iron cupferride was soluble in amyl acetate and hence iron could quickly and easily be removed by adding cupferron and extracting the insoluble salt with the organic solvent. A similar technique was employed in separating traces of copper from the nickel baths. Experiments showed that only copper was precipitated by 2-mercaptobenzothiazole in a weakly acid solution. Again, this precipitate was found to be soluble in amyl acetate and thus the copper was easily separated from the rest of the bath constituents.

The lead method utilizing dithizone illustrates a slightly different principle. The lead is not precipitated and then dissolved in an organic solvent. Instead, it is extracted with a carbon tetrachloride solution of dithizone forming lead dithizonate which immediately goes into the solvent layer. As the extraction is carried out in such a manner that only lead reacts with dithizone, lead is separated and is in a form suitable for immediate analysis all in one step.

In the procedure for cadmium, the principle of precipitation with suitable organic reagents followed by extraction of the precipitate with water immiscible solvents is first used to remove some plating bath impurities that would have interfered with the method proposed for cadmium. Then the same idea is utilized in separating cadmium from the nickel and other impurities. In this case, an interesting point is observed when 2-mercaptobenzothiazole is added to an ammoniacal solution of the bath from which copper has been previously removed, all the cadmium and an appreciable quantity of the nickel is precipitated. Although this appears to be a poor separation, it is made practically quantitative for cadmium by extracting the precipitate with chloroform and washing the extract with an ammoniacal solution of 2-mercaptobenzothiazole. The nickel complex is fairly soluble in this wash solution and is practically completely removed from the chloroform in a few extractions. Thus, use is made of the difference in the values of the distribution constants of the two mercaptobenzothiazole salts between chloroform and an aqueous solution of the organic precipitant to practically complete the separation of cadmium from nickel.

In the method developed for zinc, an organic precipitant that has not been used for this purpose before is proposed. In separating zinc from other metallic ions with dithizone, various complexing agents such as sodium thiosulfate, sodium thiosulfate plus potassium cyanide, or diethyldithiocarbamate are usually added. They form a tighter complex with the other metal ions than the latter do with dithizone and therefore the use of these complexing agents prevents their extraction by dithizone. However, the zinc dithizonate complex is much tighter than that formed with the other compounds and it is extracted by dithizone. When this technique using sodium diethyldithiocarbamate as the complexing agent is used, small amounts of cadmium are not prevented from being extracted along with the zinc and hence the separation is unsatisfactory. This difficulty can be obviated by using sodium di(-hydroxyethyl)dithiocarbamate (the sodium salt of diethanoldithiocarbamate) for complexing the other metallic constituents of the bath. This compound is closely related to diethyldithiocarbamate in structure but evidently forms a firmer complex compound with the other metallic ions than does the diethyldithiocarbamate reagent. This separation is also of interest in that it emphatically shows how fundamentally the presence of a second complexing agent can influence the reaction between metallic ions and dithizone. It would have been of interest to test the influence of other organic complexing agents on the extractability of metals by dithizone, but the time was not available.

The aluminum method involves the technique of removing the nickel by means of precipitation with sodium diethyldithiocarbamate and its extraction with chloroform. This is a new application of the precipitation and extraction technique since it is usually used to remove traces of metallic ions from solution. In this case, the major constituent of the solution is separated quantitatively in a short time from the constituent to be determined. The nickel salt of diethyldithiocarbamate is very soluble in chloroform and two extractions are enough to remove the nickel completely. This separation illustrates admirably the advantages of this type of method over a gravimetric one in which appreciable amounts of aluminum would undoubtedly have been carried down with the nickel precipitate. A point not investigated is to what extent the other elements present in the bath--copper, iron, cadmium, lead, manganese, chromium, zinc, calcium, silicates--are also removed in this extraction. It is known that copper, iron, and zinc and perhaps others of these ions also react with the reagent and may be removed along with the nickel. Indeed, this method seems likely to be a good one for removing heavy metals from aqueous solutions which are to be analyzed for the alkali and alkaline earth metals.

Methods of Determining Trace Constituents in Plating Baths

It is desirable that analytical methods developed for the routine determination of trace constituents in plating baths be of such a nature that they are rapid, do not require elaborate or expensive equipment, and may be performed by personnel that is not highly skilled or experienced in analytical chemistry.

There are many types of analytical procedures of which gravimetric, volumetric, colorimetric, polarographic, spectrographic, and electrolytic methods are the most widely used. Bearing in mind the limitations outlined above, what types of analytical methods would be most suitable for the electroplating trace? In Table I, the important characteristics an analytical method should have are indicated together with a rough estimate of how well each of the common types of analytical procedures conform to the imposed limitations.

Table I

Characteristics of Analytical Methods

Type of Method	Rapidity	Accuracy	Simplicity of Operation	Cheapness of Operation	Simplicity of Calculations	Sensitivity
Gravimetric	Low	High	High	High	Medium	Medium
Volumetric	Medium	High	High	High	Medium	Low
Colorimetric	High	Medium	High	High	High	High
Polarographic	High	Medium	Low	Low	Low	High
Spectrographic	High	Medium	Low	Low	Low	High
Electrolytic	Medium	High	High	High	High	Medium

It can be seen that colorimetric methods seem to have all the characteristic desired for this work and hence wherever possible, colorimetric procedures have been developed for trace constituent analysis in plating baths.

Since emphasis in this work is to be on colorimetric procedures, it is believed that a brief discussion of the principles underlying colorimetry or spectrophotometry is in order to clarify the experimental data given in the latter portion of this report.

When light is passed through a solution contained in a glass cell having plain parallel sides, a portion of the radiation is reflected by the sides of the vessel, some is absorbed by the solution, a little is scattered by the liquid and the remainder passes through the solution. The quantity of radiation reflected and scattered is small and constant for any given cell and hence is usually neglected.

The basic equation upon which spectrophotometry is based is known as Bouguer-Beer's Law and relates the fraction of the incident radiation transmitted by the solution to the depth or thickness of the solution and the concentration of the constituent responsible for its color.

$$I = I_o \ e^{-kbc} \quad \ldots\ldots\ldots\ldots (3)$$

where I_o = the intensity of the radiation incident upon the solution

I = the intensity of the emergent radiation from the solution

b = thickness of the solution

c = concentration of the solution

k = the specific extinction coefficient. (When the thickness is one centimeter and the concentration is expressed in moles per liter, the symbol (k) is used and is called the molecular or molar extinction coefficient.)

This relation is more commonly written as:

$$\frac{I}{I_o} = e^{-kbc} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

and $\frac{I}{I_o}$, the ratio between the intensity of the emergent and incident radiation, is called the transmittancy of the solution (T).

$\frac{I}{I_o}$ x 100 is called the % transmittancy and is one of the most widely used means of expressing this ratio.

Another commonly used form of the Bouguer-Beer equation is its Logarithmic expression:

$$\text{Log } \frac{I}{I_o} = -kbc \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

or its reciprocal

$$\text{Log } \frac{I_o}{I} = kbc \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

Log $\frac{I_o}{I}$ is called the optical density (D). Since the width of the absorption cell containing the solution is usually known, (K) is a constant and the transmittancy or extinction can be measured, the concentration of the desired constituent in the solution may be determined.

Colorimetric methods may be roughly divided into two groups:

1) Those in which the color intensity of the solution

is compared visually.

2) Those in which a photoelectric type instrument is used to measure the per cent transmittancy or extinction of the solution.

Many methods have been devised for the quantitative estimation of a desired constituent by visual comparisons. They are:

1) Standard Series Methods -- in which the color is developed in a series of standard samples so selected that their range extends from less to more than that of the unknown. The latter is then compared with each member of the series until a match is found, and the concentration of the desired constituent is assumed to be that of the corresponding standard. It is also assumed that the thickness or depth of unknown and standard is the same if they are similarly prepared solutions. Comparisons are usually made with the solutions in Nessler tubes which can be viewed vertically or horizontally with or without the use of special apparatus to make the comparison more easily. This method is probably the oldest and most widely used method and it has the advantage of being useful for solutions which do not conform to Bouguer-Beer's Law.

2) Duplication Method (Colorimetric Titration) -- The unknown is placed in a suitable container, as a Nessler tube, and the volume is brought to a given mark or depth. In a similar tube, marked for the same depth, any necessary color-forming reagents are added and nearly enough solvent to bring

the volume to the mark. From a buret, one carefully adds increments of a standard solution of the constituent being determined until, on mixing and bringing the volume exactly to the mark with solvent, the colors in the two tubes match. The amount of the constituent in the unknown is then equal to the amount present in the volume of standard solution used. As with standard series matching, the colored system need not follow Bouguer-Beer's Law.

3) Dilution Method -- The unknown is placed in a comparison tube and a known quantity of a standard solution in another. The tubes must be of the same thickness and internal diameter and be graduated for reading the volumes of solution. The more concentrated solution is diluted with solvent until, on stirring and observing the tubes horizontally, the two colors match. Then the concentrations are inversely proportional to the volumes (or depths) of the solutions and that of the unknown can be calculated. In this method, it is necessary that the colored system formed should conform to Bouguer-Beer's Law over the concentration range desired.

4) Balancing Method -- In this widely used method, the unknown and standard solution with the color developed are placed in tubes, and the depth of one fixed while that of the other is varied until the colors of the two solutions match when viewed vertically. The well known Kennicott-Campbell-Hurley comparator and Duboscq colorimeter are popular instruments which depend on this method. They each

have means by which the depth of one solution can be varied until the colors match and are good examples of the types of instruments that have been developed to make visual comparisons move accurate. As in the Dilution Method, the colored system must conform to Bouguer-Beer's Law for greatest accuracy.

In methods utilizing photoelectric type instruments, no color comparisons are involved. Instead, the fraction of the incident light absorbed by the colored system is measured and by making use of Bouguer-Beer's Law, the concentration of the desired constituent may be calculated. Because the extinction coefficient for any given color system is a constant with light of a definite wave length, it is possible to avoid the calculation and use calibration curves provided the colored solutions absorb light in accordance with the Bouguer-Beer's Law. This is done by first measuring the transmittancy or extinction of the system at different wave length of light and plotting the former against the wave length. The wave length at which the absorptance of the solute in the solution is a maximum should be used in the preparation of the calibration curves since it is obvious that greater sensitivity can be achieved by limiting the incident light to this wave length reading. This is usually done by inserting suitable filters in the path of the incident light or by using a suitably mounted grating or prism. Then the transmittancy (or extinction) of a series of samples containing known quantities of the ion to be determined are measured and the transmittancy or extinction is plotted against concentration to obtain a calibration curve. When the per cent transmittancy is measured, it should be plotted against concentration on semi-logarithym paper while if the light transmitted is measured in extinction units, the plotting is done on regular co-ordinate paper. In either case, a straight line will be obtained if the colored system developed conforms to the Bouguer-Beer's Law.

Photoelectric instruments for measuring the transmittancy of colored solutions can be divided into two classes:

1) Filter photometers (abridged spectrophotometers) -- In these instruments, colored glass filters are used to obtain a spectral band which although relatively wide can still be used for routine work. It is important in order to obtain maximum sensitivity for the determination to use a filter whose transmitted spectral band corresponds as closely as possible to the spectral region of the solution's maximum absorptance. For example, the colored complex formed by ferrous iron and 1,10-phenanthroline shows a maximum absorptance around 508 millimicrons. Hence, for best results, a filter showing maximum transmittancy for light around this wave length should be used.

Typical of this type of instrument is the Cenco-Sheard-Sanford filter photometer manufactured by the Central Scientific Company whose principal functional parts are shown in Figure 1.

(S) is an ordinary small incandescent lamp the voltage for which is provided by the constant voltage transformer (T). The light passes through the Iris diaphram (I), the lens (L) which transmits the light in parallel beams into the absorption cell (A) containing the colored solution, through the glass filter and finally impinges upon the photovoltaic cell (P). The current generated by the photovoltaic cell is measured on the microammeter (M) which is calibrated to read 0 to 100% transmittancy.

Another type employing two photoelectric cells is the Klett-Summerson colorimeter shown in Figure 2. (A) is a 100 watt projector lamp and (F) is a glass filter through which the light passes to the compensating lens (L_1) and (L_2). The emerging, parallel beams of light pass through the testtube cell (C)--cells with plane parallel sides are also available--and then impinge on the photoelectric cell (P_2). The light passing through lens (L_2) does not pass through any cell, but falls directly on the photoelectric cell (P_1). The current from the photoelectric cell (P_2), which is a measure of the light transmitted by the solution, deflects the galvanometer needle and the resistance (P) is varied to bring the galvanometer needle back to its original or zero position. The resistor (P) has an attached scale which is calibrated in units proportional to the extinction of the solution under examination.

This instrument has the advantage over the one cell instrument described earlier in that the incident light is split into two beams and hence any fluctuations in the line voltage affect both beams equally and since they buck each other via the photoelectric cells, the effect of the voltage fluctuation does not affect the readings obtained. With a one cell instrument, such fluctuations are not compensated for in any way and hence the colorimeter must be readjusted again before a reading can be taken.

2) Spectrophotometers

These instruments have either gratings or prisms for diffracting light from a projector lamp and different portions of the spectrum can be brought into position to pass through a slit by turning a wave length dial. Thus, more nearly monochromatic light can be obtained than is possible with the use of ordinary glass filters. With some instruments, a wave band around 2 to 5 millimicrons in width can be obtained while with others a band about 30 millimicrons passes through the slits and then through the colored solution.

One of the best of these instruments is the Beckman ultraviolet spectrophotometer manufactured by the National Technical Laboratories, a sketch of whose optical parts is shown in Figure 3. An image of light source (A) is focused by the condensing mirror (B) and the diagonal mirror (C) on the entrance slit at (D). The entrance slit is the lower of two slits placed vertically over each other. Light falling on the collimating mirror (E) is rendered parallel and reflected towards the quartz prism (F). The back surface of the prism

Fig. 2.

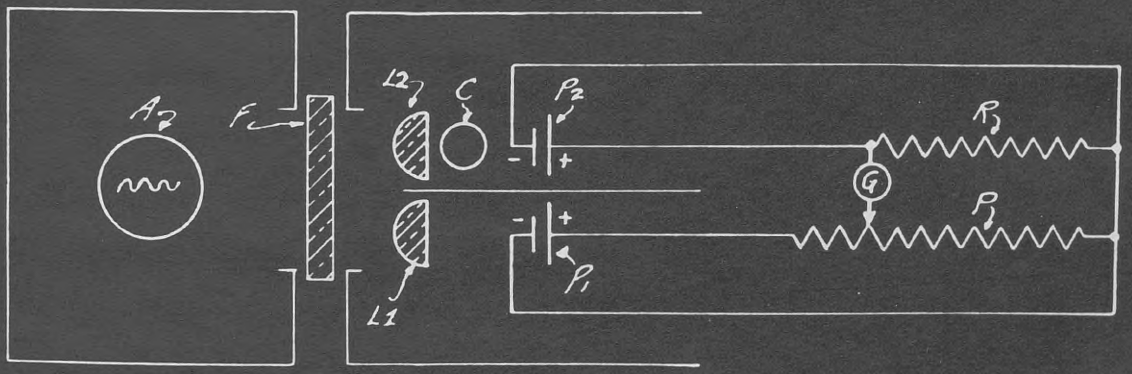
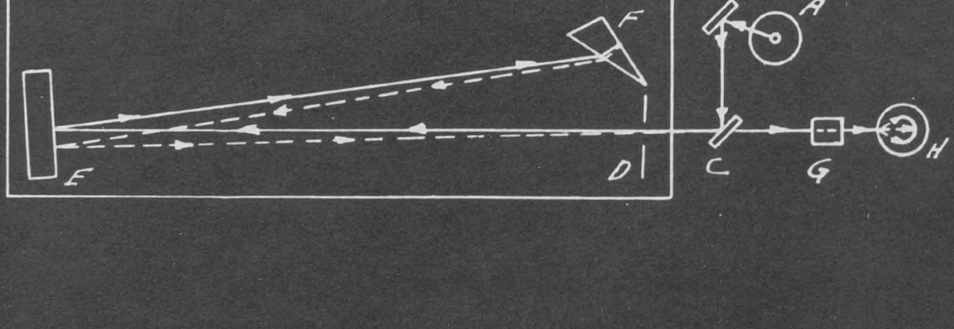


Fig. 3.



is aluminized so that light refracted at the first surface is reflected back through the prism, undergoing further refraction as it emerges from the prism. The collimating mirror (E) focuses the spectrum in the plane of the slits (D) and light of the wave length for which the prism is set passes out of the monochromator through the exit (upper) slit, through the absorption cell (G) containing the colored solution to the photoelectric cell (H). The current generated by the photoelectric cell is bucked by a potentiometer arrangement whose resistor is calibrated to give readings in extinction or per cent transmittance. The instrument can also be used for work in the ultraviolet region of the spectrum with quartz cells available for holding the sample.

Knowing what types of instruments can be purchased and what can be done with them is of great importance in enabling one to select a spectrophotometer that will be suitable for the purpose at a reasonable cost. Thus, it a concern is only interested in purchasing an instrument for routine work, it is a waste of money to purchase a Beckman spectrophotometer which costs in the neighborhood of $1500. The results would be more accurate, but the added accuracy is not too important in strictly routine operation. Also, if one is planning to develop colorimetric methods, it would be advisable to get a more expensive instrument than the Cenco-Sheard-Sanford or the Hellige-Diller instrument. The purchase of a Beckman is only justified if one is interested in doing work in the ultraviolet, at longer wave length (above 600 millimicrons), want to obtain very accurate spectral transmittance curves, or wishes to get results of the greatest possible accuracy.

In developing colorimetric methods for the plating industry, this matter was considered at some length. It was felt that most companies wanted methods for routine control work and since the majority of the electroplating plants are not large establishments, they could not afford an expensive instrument. Moreover, the instrument had to be easy to operate since technically trained men were not available in many plating concerns. Therefore, it was decided to develop all methods using the Klett-Summerson colorimeter. This seemed to be a good, relatively inexpensive instrument that any non-technical person could learn to run in a short time.

Methods of Analysis

It is the purpose of this brief discussion on methods of separating trace quantities of material, types of analytical methods, and on the principles of spectrophotometry, to outline the purpose and scope of the work and the means by which it has been successfully concluded. The analytical methods developed for lead, iron, manganese, copper, cadmium, chromium, zinc, and aluminum in nickel plating baths will not be described.

Summary

Analytical methods for the determination of trace amounts of lead, iron, manganese, copper, cadmium, chromium, zinc, and aluminum in nickel plating baths have been developed. Special emphasis has been given to the use of new methods of separating these traces from the bath by the use of organic precipitants and the extraction of these complex compounds with organic solvents. The methods developed are all colorimetric procedures designed to be used by routine analysts who have had little chemical training. The methods as soon as completed have been sent out to cooperating industrial laboratories for checking. Before these procedures are published, they are checked for their accuracy and modified in accordance with any comments and suggestions made by the checking laboratories. Thus, these methods are thoroughly checked and rechecked before being offered to the electroplating industry for use.

SECTION A

THE DETERMINATION OF LEAD IN NICKEL PLATING BATHS

THE DETERMINATION OF LEAD IN NICKEL PLATING BATHS

The purpose of this investigation was to develop a rapid, accurate method for the determination of very small amounts of lead in nickel plating baths which also contain appreciable quantities of aluminum, cadmium, copper, iron, manganese, calcium, silicon, zinc, and chromium.

It was also desirable to restrict the method selected to one which does not involve the use of costly equipment or the employment of a well trained and experienced chemist.

These limitations led to the search for a spectrophotometric method. The apparatus required is inexpensive, does not require the services of an experienced chemist, and the results are both rapid and fairly accurate.

From a survey of the literature, the method which seemed most likely to give satisfactory results is the dithizone method first used by Fischer and Leopoldi (33).

The electrolytic separation of lead as lead dioxide, PbO_2 (85, 4, 99), and its oxidation of tetramethyldiaminodiphenylmethane to the intensely blue colored diphenylmethane dye was studied (126). The method is simple and rapid, but it is not as accurate as the dithizone method especially for small amounts of lead--10 gamma or less. Any other peroxide like manganese dioxide, MnO_2, that might possibly be deposited along with the lead dioxide, PbO_2, will oxidize the reagent. Furthermore, the color is not very stable.

Lead can be determined indirectly by precipitating it as lead chromate, dissolving the thoroughly washed precipitate in acid, and determining the amount of chromate present with s-diphenyl carbazide which forms an intense red-violet colored solution (64, 65). However, the method was known to give low results (65, 15), and was not considered further.

Since its introduction, the dithizone method has been used extensively for the determination of lead in biological materials (15, 59), water (99), silicate rocks (95), and in many other substances.

Many elements besides lead react with dithizone to form colored complex compounds (96), namely, manganese, iron, nickel, cobalt, copper, zinc, palladium, silver, cadmium, indium, tin, platinum, gold, mercury, thallium, and bismuth. However, when potassium cyanide is added to a slightly alkaline solution in quantities sufficient to form complex cyanides with all the metallic ions present, lead, bismuth, thallium, and stannous tin are the only elements that can react with dithizone. Since bismuth, thallium, and stannous tin are not usually present in nickel plating solutions, lead may be isolated by this means from all the other elements in the bath. If it is necessary to separate lead from these metals, methods are available for doing so (132, 39, 58, 87).

The lead separation is satisfactory only when the pH is properly adjusted and enough potassium cyanide has been added to complex all the metallic ions present, with less, some of the other metals in the solution will be extracted with the lead--usually nickel. The importance of this point is illustrated by the amounts of potassium cyanide required when runs are made on a Watts type nickel plating bath without and with impurities added. The former requires 8.5 ml. of 5% potassium cyanide solution. The same amount added to the same quantity of the bath containing impurities is not enough. Even after ten extractions with dithizone had been made lead was still present in the aqueous phase. Since only three of four extractions are required to remove the same amount of lead from the pure bath and the pH of both solutions were the same, it is evident that some other metal is being extracted along with the lead. When 12 ml. of the potassium cyanide solution was added, 3 or 4 extractions removed all the lead. However, one must be careful not to add too great an excess of potassium cyanide as it too will increase the number of extractions required.

As noted above, the pH of the solution from which lead is to be extracted must be carefully controlled. Clifford and Wichmann (20) studied the extractability of lead at various acidities. Using a chloroform solution of dithizone, they found the optimum pH range to be about 8.0 to 10.0. With a carbon tetrachloride solution of dithizone, the optimum range was about 8.0 to 10.0. Below 8.0, many extractions were necessary and above the upper limit, the lead dithizonate decomposed. In this investigation, it was found necessary to confine the pH range between 8.5 and 9.0 in order to keep the number of extractions to a minimum.

After the lead has been isolated, there are a number of ways in which the quantity of lead may be determined (98).

(1) The Mono-color Method (98,17, 38). The excess dithizone in the lead extractions is removed by shaking the extracts with a dilute ammonia-potassium cyanide mixture. After dilution of the lead dithizonate with pure solvent to a definite volume, its transmittancy is measured either by means of a spectrophotometer at 520 millimicrons wave length or a filter photometer with a filter which provides maximum transmission around this wave length. The lead concentration is then obtained from a calibration curve. As an alternative the pure lead dithizonate can be decomposed by making the solution slightly acid, and the transmittancy of the green organic solvent layer determined after dilution to a suitable volume at 610 millimicrons or by using a filter with maximum transmission around this wave length.

(2) The Mixed Color Method (3, 59, 20, 21, 98). In this method, the lead dithizonate is decomposed by adding dilute acid, throwing away the organic solvent layer, adjusting the pH to about 9.5 with ammonium citrate or tartrate adding potassium cyanide, and shaking the solution with a definite excess of dithizone solution of known concentration. The organic layer will have a blue or red violet color depending on the amount of excess dithizone and the amount of lead.

The determination is made by measuring the amount of light transmitted by the solution at 520 millimicrons which is the wave length at which lead dithizonate shows maximum absorption or at 610 millimicrons, the wave length at which dithizone absorbs light strongly. The latter method is the more accurate because the lead dithizonate shows little light absorption above 600 millimicrons, while dithizone absorbs appreciably at 520 millimicrons. It does, however, require closer pH control.

(3) The Standard Series Method (98). This is a visual method of estimating the amount of lead present. As in the mixed color method, the lead is isolated, transferred to the aqueous layer and shaken with a measured excess of dithizone solution. At this point, the organic layer is transferred to a glass stoppered tube and its hue is compared to those of a series of solutions containing known amounts of lead and the same amount of dithizone placed in similarly prepared tubes.

(4) Colorimetric Titration (98). This method does not make use of a series of standards. Instead, to one tube containing the same amount of all reagents except lead as the unknown, a standard solution of lead is added from a micro burette until the mixed color of the standard matches that of the unknown.

For this investigation, the mono-color method has been selected in which the light absorbed by the lead dithizonate at 520 millimicrons is measured since it is the most rapid and is capable of giving results accurate to 1 gamma when properly carried out (20). In 1944, a similar method for lead in plating baths was described by Foulke (42).

Experimental

From a study of the previous work done on the determination of lead with dithizone and the results obtained from our own preliminary experimental work, a routine procedure was developed based upon the separation of lead from interfering ions by extraction with a carbon tetrachloride solution of dithizone in the presence of potassium cyanide. After removal of the excess dithizone with alkaline potassium cyanide, the transmittancy of the solution is measured and the quantity of lead present determined from a calibration curve. The detailed recommended procedure appears at the end of this paper.

The experimental work done was divided into three parts:

1) preparation of a transmittancy versus wave length curve for lead dithizonate dissolved in carbon tetrachloride.
2) preparation of a calibration curve relating transmittancy to concentration of lead using the recommended routine procedure.
3) determination of the accuracy and the precision of the proposed method.

Preparation of the Transmittancy Versus Wave Length Curve

A solution of lead dithizonate in carbon tetrachloride containing 20 micrograms of lead per milliliter was prepared and a portion placed in the cell of a Beckman spectrophotometer. The curve obtained by plotting the transmittancy against the wave length is shown in Fig. (1). It will be noted that the solution absorbs strongest at about 520 millimicrons.

Fig. (1) also shows the transmittancy versus wave length curve--(curve b)--for the Klett-Summerson green filter #54 recommended in the procedure. It will be noted that the wave length range over which its transmittancy is a maximum corresponds to the wave length at which the lead dithizonate absorbs the strongest. When the maximum transmittancy of the filter used approximately coincides with the wave length at which a solution shows maximum absorption, the use of a filter will result in the greatest sensitivity of the method.

Preparation of the Calibration Curve

The data shown in Table I was obtained when the recommended routine procedure was followed in adding varying quantities of the standard lead solution to one milliliter of a synthetic Watts type plating bath.

Table I

Calibration Curve Data

Gamma Pb Added	Corrected Readings	Average Readings	Mean Av. Reading
5	36-37-35	36	36
5	29-38-36	38	
5	35-31-34	33	
10	64-61-58	61	67
10	67-64-64	65	
10	77-74-75	75	
20	142-132-136	137	137
20	145-140-136	140	
20	136-134-135	135	
30	197-195-196	196	204
30	220-219-212	217	
30	204-200-195	200	
40	252-254-245	250	258
40	265-252-280	268	
40	265-240-258	255	
50	360-345-325	344	334
50	335-330-325	330	
50	325-330-330	328	

The calibration curve shown in Fig. (2) was obtained by plotting the mean average readings against the corresponding lead content of the solutions.

The straight line obtained shows that Bouguer-Beer's Law is obeyed by lead dithizonate dissolved in carbon tetrachloride over the concentration range tested. The molar extinction coefficient of the solution was found to be fairly constant with varying amounts of lead as it should be if Bouguer-Beer's Law is obeyed. The average value of the molar extinction coefficient was 8.29×10^4 at a wave length of 520 millimicrons.

Determination of the Accuracy and the Precision of the Method

To check the accuracy and precision of the method under conditions that will usually be met with in industrial practice, other metallic ions were added to 100 ml. of the synthetic Watts bath which had been used in preparing the calibration curve. This solution was then used in the tests.

Table II shows the ions and the amounts which were added to the pure bath. Solid soluble nitrates, chlorides, or sulfates of the various metals were used wherever possible.

Table II

Kind and Amount of Impurities Added

Metal Ion	Amount Added (mgs.)	Equivalent in grams/l. bath
Aluminum	100	1.0
Cadmium	100	1.0
Chromic oxide (CrO_3)	20	0.2
Copper	20	0.2
Manganese	100	1.0
Iron	100	1.0
Silicon	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

All salts dissolved readily except the 200 mgs. of calcium chloride added. The solution was heated, shaken vigorously, cooled, shaken well again and then filtered.

The filtrate was used for the tests.

The same procedure was followed as that used in the preparation of the calibration curve. Table III shows the results procured in checking the accuracy obtained on single runs. When the procedure is closely followed, the method will give an accuracy of better than 10%.

Table III

Data Showing Accuracy of the Method

Gamma Pb Added	Corrected Readings	Average Reading	Gamma Lead Recovered
5	33-34-36	34	5.0
10	60-67-66	65	9.5
20	162-160-140-150	153	20.5
40	275-295-290-270	282	41.3
50	325-325-330	327	48.0

In order to further check the accuracy of the method, enough lead was added to the synthetic plating bath used above so that each milliliter of the bath contained 20 micrograms of lead. A portion of this solution was analyzed for lead by the writers and samples were sent to the Bethlehem Steel Corporation, Bethlehem, Pa.; Foster D. Snell, Inc., Brooklyn, New York; and Bell Telephone Laboratories, New York, New York. These companies had kindly consented to test the procedure described in this paper.

The results obtained by the various laboratories are presented in Table IV.

Table IV

Results from Cooperating Laboratories

Laboratory	Micrograms of Lead/ml.
Foster D. Snell, Inc.	21.0
Bethlehem Steel Corp.	22.3
Bell Telephone Laboratories	20.5
Lehigh University	21.0

To test the precision of the method, six duplicates containing 20 gamma of lead were run. The results are shown in Table V.

Table V

Precision of Method

Gamma Pb Added	Corrected Readings	Average Reading	Gamma Lead Recovered
20	156-136-141-138	143	20.5
20	149-147-139	145	20.5
20	141-139-137	139	20.0
20	157-153-151	154	22.0
20	143-151-138	142	20.2
20	152-150-130-140	143	20.5

The precision is fairly good, but only if details are followed exactly.

Recommended Routine Procedure

Reagents Required:

1) Dithizone solution . . . . 0.1g/l.

The commercial dithizone usually purchased has a purity of 80-90%. The main impurity is an oxidized form of dithizone called diphenylthiocarbodiazone which interferes in most dithizone methods. In carbon tetrachloride, it forms a yellow to brown solution which may alter the transmission of the solution under examination. Hence, it is desirable to remove as much of it as possible. In the purification of the dithizone solution, advantage is taken of the fact that the diphenylthiocarbodiazone is not soluble in a basic solution while dithizone is soluble.

To purify, (17, 97) dissolve 100 milligrams of the reagent in 50 ml. of carbon tetrachloride and filter off any insoluble matter catching the filtrate in a 150 ml. Squibb type separatory funnel. Add 50 ml. of a (1:100) solution of NH_4OH and shake for about one minute. After the liquids have separated, run the carbon tetrachloride layer into another separatory funnel containing 50 ml. of the (1:100) NH_4OH and shake again. This second extraction will remove practically all the dithizone from the carbon tetrachloride layer. It should be colorless or have a light green color at this point. Discard the carbon tetrachloride layer and combine the two aqueous NH_4OH extracts. Wash these extracts four times with 10 ml. portions of carbon tetrachloride. This will take out any diphenylthiocarbodiazone present. Now precipitate the dithizone with 2 ml. of concentrated HCl and shake for a minute. Finally, extract the precipitated dithizone with 25 ml. portions of carbon tetrachloride until the aqueous layer is colorless. Run these extracts into a pyrex liter flask and dilute to one liter with carbon tetrachloride. To protect the solution against oxidation, overlay it with a 5% solution of pure hydroxylamine hydrochloride one centimeter thick. Keep the solution in a cool, dark place. It is stable for several months if kept in a refrigerator.

2) Potassium cyanide solution 5%

Dissolve 50 grams of the fresh salt in sufficient water to make a liter of solution. Keep the solution in a pyrex flask or bottle.

3) Alkaline potassium cyanide solution.

Mix 10 ml. of the above 5% KCN solution and 5 ml. of concentrated NH_4OH and dilute to one liter.

4) Sodium tartrate solution 10%

Dissolve 100 grams of the salt in distilled water and dilute to a liter.

5) Concentrated ammonium hydroxide . . . . . . c.p. grade

6) Tartaric acid 50%

Dissolve 25 grams of tartaric acid in distilled water and dilute to 50 ml.

7) Thymol blue indicator.

The indicator is used if a pH meter is not available.

8) Synthetic Watts type nickel plating bath.

Three hundred and thirty grams $NiSO_4 \cdot 7H_2O$, 45 grams $NiCl_2$, 30 grams H_3BO_3 are dissolved in pure distilled water to make one liter.

(a) Standard Lead Solution -- 10 micrograms/milliliter.

Dissolve 100 milligrams of pure test lead in 2 ml. of HNO_3. The lead nitrate is transferred to a liter flask with thorough rinsing of the 50 ml. beaker in which the lead is dissolved. Add 5 ml. of glacial acetic acid, dilute to the mark with lead free water and mix well. Dilute 10 ml. of this solution to 100 ml. The diluted solution contains 10 gamma of lead per ml. Lead acetate or lead nitrate may be used for preparing the standard lead solution, but because of uncertainty in regard to the amount of moisture and water of crystallization the salts may contain, it is best to use pure lead.

<u>Apparatus required</u>:

1) pH meter or its equivalent.

2) Two 60 - 100 ml. short stemmed separatory funnels (Squibb type).

3) Pipettes and burettes.

4) Colorimeter -- Klett-Summerson with green filter #54 or any other photoelectric colorimeter.

<u>Procedure</u>:

For routine control work, the following procedure should give satisfactory results if closely followed.

Adjustment of the pH:

1) Transfer 1 ml. of the plating bath to a separatory funnel (Note 1).

2) Add 10 ml. of the sodium tartrate solution.

3) Add 6 drops of concentrated NH_4OH -- more if needed. (Note 2).

4) Add potassium cyanide from a burette until the solution is straw colored--with the usual amounts of impurities present, 12-13 ml. should be enough. If the nickel bath contains more nickel than the bath used in this investigation, increase the amount added. If there is any trace of a greenish color, add more reagent.

5) Measure the pH of the solution with a pH meter and if it is not between 8.5 and 9.0, add tartaric acid or NH_4OH from a dropping bottle until it is properly adjusted. If thymol blue indicator is used, add 5 drops of it at this point and adjust the acidity until the solution is greenish in color.

Isolation of the Lead:

6) After the pH has been adjusted, add 5 ml. of dithizone solution from a burette, shake for 30 seconds, allow the layers to separate, and run the solvent layer into another clean separatory funnel.

7) Repeat the extraction with 2 ml. portions of dithizone until the dithizone remains green in color. This indicates that all the lead has been extracted.

8) Add 5 ml. of pure carbon tetrachloride and again shake for 30 seconds. Combine this extraction with those made with dithizone.

9) Add 20 ml. of alkaline potassium cyanide solution to the combined extracts.

10) Shake for 30 seconds, allow layers to separate, and draw off the carbon tetrachloride layer into a 25 ml. volumetric flask.

11) Dilute this solution with pure solvent to the mark and shake well.

Measurement of the Transmittancy of the Lead Dithizonate:

12) Filter the solution through a clean Whatman No. 40 paper moistened with carbon tetrachloride. Catch the filtrate in a clean dry erlenmeyer flask. (Note 3).

13) After the instrument has been adjusted with pure carbon tetrachloride as the reference liquid, transfer a portion of the filtrate to a matching testtube. Rotate the dial until the galvanometer needle returns to the zero position and record the scale reading. If the instrument used has a wave length scale, set it for 520 millimicrons.

14) Run a blank going through the above procedure with the same number of dithizone extractions as were required to extract the lead. Record the scale reading of the blank. (Note 4).

15) Subtract the blank reading from the sample reading. Record this corrected scale reading and on the calibration curve, read the amount of lead in the sample taken for analysis. (Note 5).

Notes on Recommended Routine Procedure

Note (1). The calibration curve is prepared for amounts of lead up to 50 gamma per 25 ml. of solution. This is equivalent to 2 ppm. If tests show that more than this amount of lead is present, a smaller aliquot of the plating bath must be taken. This can be done by using a pipette graduated in fractions of a milliliter or by diluting 1 ml. of the plating bath to 50 or 100 ml. and then taking a suitable aliquot of this diluted solution. In any event, the aliquot taken for analysis should not contain more than 50 gamma of lead unless the calibration curve is extended.

Note (2). If 6 drops of ammonium hydroxide is not enough to make the solution distinctly ammoniacal, add more. Avoid a large excess.

Note (3). The purpose of the filtration is to remove water droplets that are suspended in the carbon tetrachloride layer. If this is not done, droplets are soon found on the sides of the testtube cell and will likely affect the light transmittancy of the solution. Filtration does not seem to affect the lead color in any way.

Note (4). In running the blank, it is essential to use as many extractions with dithizone as in running the regular sample. The reading of the blank increases as the number of required extractions increase. This may be due to the incomplete removal of the excess dithizone by the alkaline KCN or by the presence of some diphenylthiocarbodiazone despite purification. It is quite possible that some substances present may also oxidize the dithizone. Ferric iron for example readily oxidizes it. This method of correcting for the blank can only be employed when the instrument has an extinction scale or one related to the extinction as explained in the general notes.

Calculations:

Suppose that the corrected scale reading is 258. According to the calibration curve, the reading corresponds to 40 gamma of lead. If one ml. of the bath is taken for analysis, then 40 x 1000 = 40,000 gamma or 40 ppm of lead is present in the bath. This is equal to 0.040 grams per liter.

If the solution is known to transmit light in accordance with Bouguer-Beer's Law and the instrument has a logarithmic scale, it is possible to eliminate the need for a calibration curve.

An example will make the method clear. Run an unknown and a standard sample, simultaneously treating each exactly the same. Get their scale readings and correct for blanks as described above. Since the readings for both the standard and unknown are directly proportional to the concentration-- if the Bouguer-Beer's Law holds--the concentration of the unknown is calculated by the use of the following formula:

$$\frac{\text{Concentration of Standard}}{\text{Corrected Reading of Standard}} \times \text{Reading of Unknown} = \text{Concentration of Unknown}$$

Suppose, the standard contains 20 gamma of lead and has a corrected reading of 137. The unknown--using 1 ml. of plating bath--gives a corrected reading of 175. Substituting these numbers into the above formula, the amount of lead in 1 ml. of the bath under test is 20/137 x 175 = 25.9 gamma. Hence, in one liter there is 25.9 x 1000 = 25,9000 gamma = 25.9 ppm or .0259 grams of lead per liter.

Once the standard is run, it is not necessary to run it with each unknown although it would be desirable since $\frac{\text{concentration of standard}}{\text{corrected reading of standard}}$ is a constant. It would only be necessary to multiply the scale reading of an unknown by this constant factor to get the concentration of lead in the unknown.

A "Stop and Go" Method for Lead

A "Stop and Go" method may be roughly defined as one that in a short time will give the analyst an approximate idea of the amount of lead in the solution.

If the pH of the solution has been adjusted correctly, the number of extractions required to remove all the lead can serve as a "Stop and Go" method.

"Stop and Go" Procedure for Lead:

1) Follow the recommended routine procedure up to and including step (5).

2) After the pH has been adjusted, add 2 ml. of dithizone solution from a burette, shake for 30 seconds, allow the

liquid layers to separate, and run the lower layer into another clean separatory funnel.

3) Continue the extractions with 1 ml. portions of dithizone recording the number of extractions required including the first one until the dithizone remains green in color.

4) The amount of lead present in the sample can be estimated by reference to Table VI.

Table VI

Estimation by Appearance of Extract

No. of Dithizone Extractions	Gamma of Lead Present	Notes
2	10	
3	20	2nd extraction is almost green
3	30	2nd extraction definitely purple
4	40	3rd extraction almost green
4	50	3rd extraction definitely purple

Note (a). It must be emphasized that this method will work only if the pH of the solution is between 8.5 and 9.0.

Note (b). By noting the various shades of purple of each extract, an operator will quickly be able to estimate the lead content of a sample within 10 gamma without much difficulty.

Summary

A method for the determination of lead in nickel plating baths is described. The lead is separated from interfering ions by extraction with a carbon tetrachloride solution of dithizone in the presence of potassium cyanide. After removal of the excess dithizone with alkaline potassium cyanide, the transmittance of the solution is measured and the quantity of lead present determined from a calibration curve.

FIGURE (1)

(a) - Extinction versus wave length for lead dithizonate --20 ppm--in carbon tetrachloride.

(b) - Extinction versus wave length for Klett-Summerson filter #54. The extinction units to the right apply to this curve.

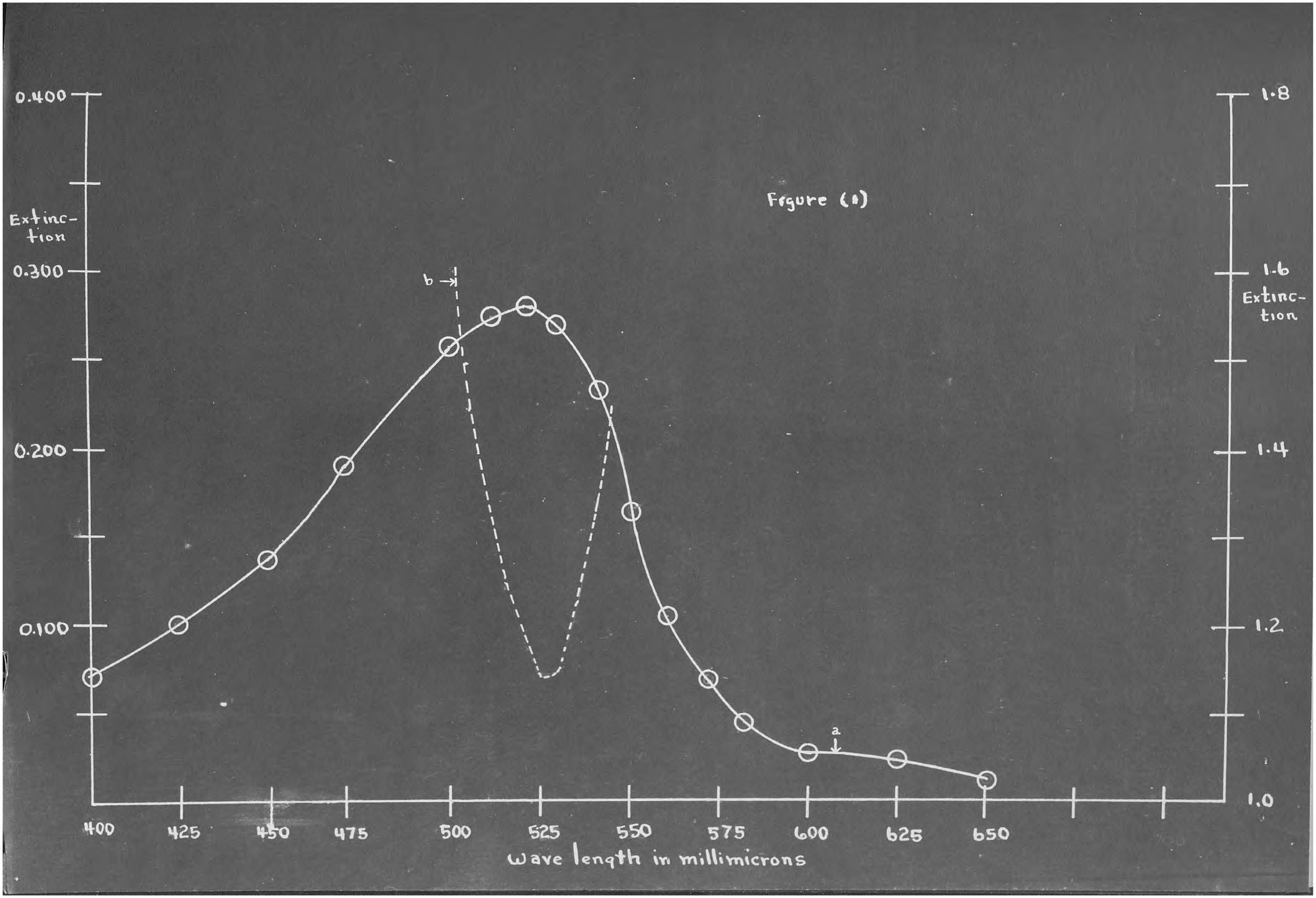


Figure (8)

0.400
Extinc-tion
0.300
0.200
0.100
1.8
1.6
Extinc-tion
1.4
1.2
1.0
b →
a
400
425
450
475
500
525
550
575
600
625
650
Wave length in millimicrons

FIGURE (2)

Calibration curve for the determination of lead in a Watts type nickel plating bath using dithizone.

Instrument used -- Klett-Summerson colorimeter with green filter #54.

Type of cell -- testtube.

Final Volume of Solution -- 25 ml.

Slope of Curve -- 0.148 gamma Pb/scale reading.

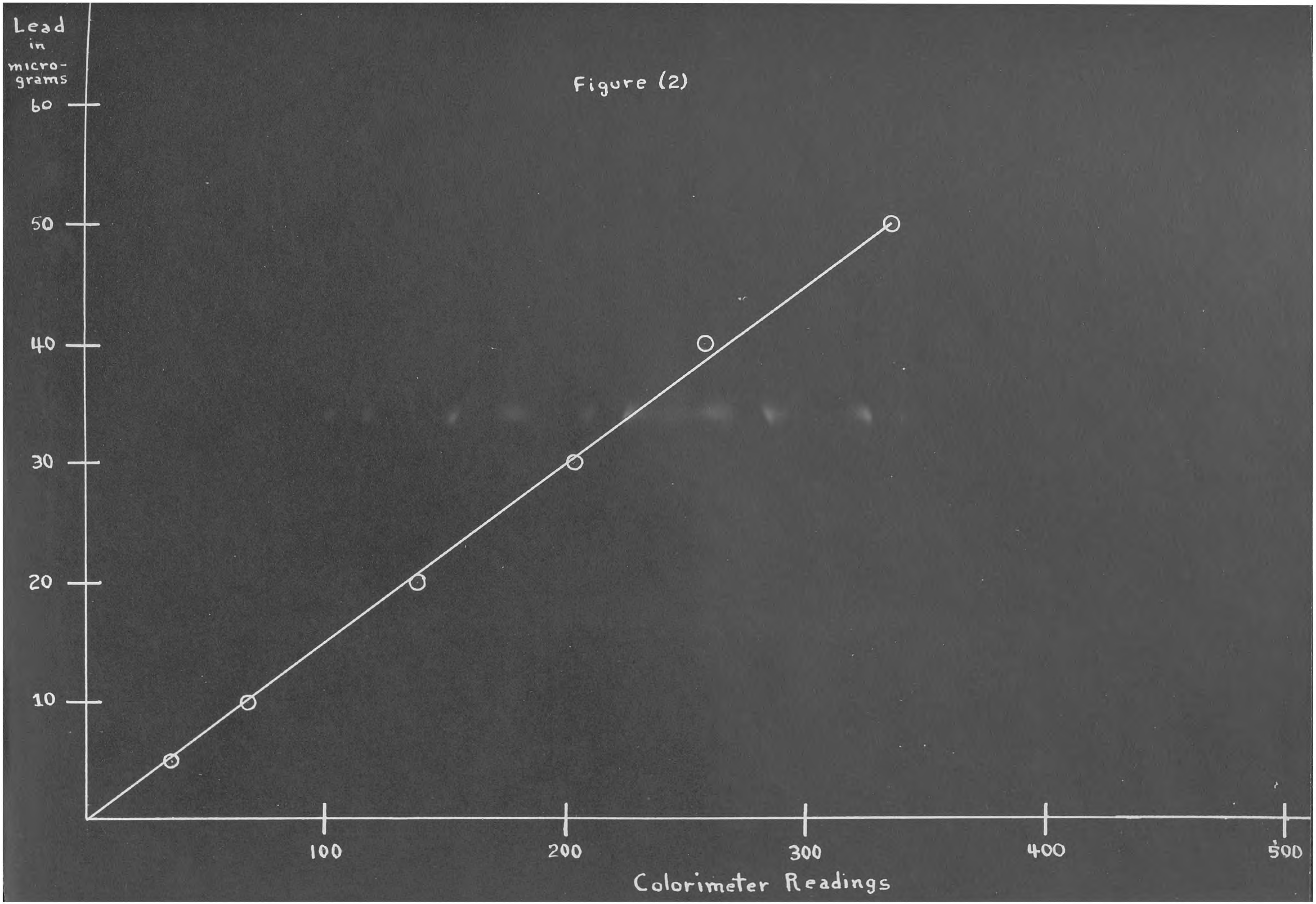


Figure (2)

Lead in micro-grams
60
50
40
30
20
10
100
200
300
400
500
Colorimeter Readings

SECTION B

THE DETERMINATION OF IRON IN NICKEL PLATING BATHS

THE DETERMINATION OF IRON IN NICKEL PLATING BATHS

The purpose of this investigation is to develop a rapid, accurate method for the determination of very small amounts of iron in nickel plating baths which also contain appreciable quantities of aluminum, cadmium, copper, lead, manganese, silicon, zinc, calcium, and chromic oxide (CrO_3).

A literature search indicated that little work had been done on the subject. Thompson and Thomas (123) determined iron in nickel salts used for preparing nickel plating baths by precipitating the iron with NH_4OH and igniting the filtered hydroxide. Linick (73) and Foulke and Horner (44) used the reaction between ferric iron and potassium thiocyanate to colorimetrically determine iron in nickel plating baths.

A rapid, fairly accurate method that did not require expensive equipment or the employment of skilled personnel was desired. Since colorimetric methods seemed to fit these qualifications best, the various colorimetric methods for the determination of iron were studied.

There are many reagents available which form highly colored solutions with ferrous or ferric iron (115, 117, 135). However, few are good for determining traces of iron. For ferric iron, the reaction with thiocyanate seems to be in greatest usage. Ferric iron reacts with potassium thiocyanate in acid solution to give a red complex ion whose composition is uncertain. The method, despite the instability of the color and the many interfering substances enjoys great popularity because of its sensitivity and simplicity (6a, 88, 102, 135). Of the reagents that form colored complexes with ferrous iron, O-phenanthroline,

-bipyridyl, and 2,2',2"-terpyridyl seem to be the best for colorimetric work. They form red colored complexes in slightly acid solutions that are very stable (6-12 months), very sensitive, and do not require close pH control (115, 103, 84, 60, 41).

For this investigation, the reaction between ferrous iron and O-phenanthroline seemed most likely to give satisfactory results, and an effort was made to apply it to the determination of iron in nickel plating baths.

In order to familiarize the reader with the conditions under which the ferrous iron ortho-phenanthroline color is developed and the effect of various ions on it, a brief summary of this material follows.

The reaction between ferrous iron and O-phenanthroline in slightly acid solutions results in the formation of an orange-red complex having the formula $(C_{12}H_8N_2)Fe^{++}$. Plotting the transmittancy of this color against the wave length of the incident light (41, 115) shows that the complex ion exhibits maximum transmittancy at a wave length of 508 millimicrons. The color intensity of the complex is independent of the acidity in the pH range 2-9. Below a pH of 2, the color develops slowly and is much weaker. However, the presence of certain ions alter the pH range that can be used. The advantage of being able to work around a pH of 2 is that one need not be concerned with the possible precipitation of metallic hydroxides and phosphates.

Of all the 55 ions tested by Fortune and Mellon (41) for their effect upon the intensity and transmittancy of the iron complex, only silver and bismuth--which form precipitates with the reagent--must be absent.

Calcium, lead, manganese and aluminum can be present in amounts up to 500 ppm without causing an error of more than 2%. With sufficient excess of O-phenanthroline, up to 50 ppm of cadmium and 10 ppm of zinc can be tolerated without appreciable error. Nickel changes the hue and hence the transmittance of the solution. Only about 2 ppm of nickel can be present without interference. Ten ppm of copper, 20 ppm of chromate, and 100 ppm of silicate are the maximum amounts of these ions that can be present. For a more complete discussion of the effects of these and other ions, the reader should consult the paper by Fortune and Mellon (41).

Developmental Work

In view of the varying quantities of nickel and other elements in commercial baths, it seemed advisable to find a way to separate the iron from all or most of the constituents present and then develop the colored system.

If cupferron is added to a dilute acid solution, small amounts of iron can be quantitatively precipitated without precipitating any of the other bath constituents except possibly a portion of the copper (8, 7, 75, 116). To separate the small quantity of iron cupferride formed from the rest of the mixture, solvent extraction seemed to be more practical than filtration. Hence, a number of water immiscible solvents were tested to find out which ones would dissolve iron cupferride. Of those tried, amyl acetate seemed to give the best results. Therefore, by adding cupferron to an aliquot of the bath and extraction the cupferride with amyl acetate, the iron can be quantitatively separated from the bath.

The next problem encountered is to find some way of getting the iron dissolved in the amyl acetate back into the aqueous medium. This can be done by vigorously shaking the amyl acetate extract with (1:1) HNO_3.

The iron, following this treatment is in the ferric state and free of interfering ions. The colored system can now be developed in the usual manner by reducing the ferric iron with hydroxylamine hydrochloride, adding O-phthanthroline, and finally adjusting the acidity by adding sodium acetate. If the pH is adjusted properly, the maximum color will develop almost instantly. The transmittancy of the solution can be measured as soon as the solution is diluted and mixed.

The order in which the reagents are added is not of particularly great importance. Fortune and Mellon (41) add the sodium acetate first and then the reducing agent and O-phenanthroline. Hummel and Williard (60) do likewise. However, Bandener and Schaible (5) showed that the results are somewhat more duplicable when the order described above is used. Such was also the writer's experience.

Various reagents have been used to reduce the ferric iron to the ferrous state. Fortune and Mellon (41) use hydroxylamine hydrochloride after testing the usefulness of sodium sulfite, sodium formate, potassium formate, and formaldehyde--all of which did not give satisfactory results. Hummel and Williard (60) use hydroquinone.

Preliminary Procedure Tests

On the basis of the above results, a tentative procedure was outlined. The iron can be precipitated with cupferron and the cupferride extracted with amyl acetate. The iron is returned to an aqueous media by shaking the amyl acetate solution with (1:1) HNO_3. Then the iron-O-phenanthroline color is developed by the addition of hydroxylamine hydrochloride, O-phenanthroline and sodium acetate respectively to the nitric acid solution.

The question now arose as to whether small amounts of iron--say 10 micrograms--could be completely recovered by the proposed method.

As a criterion for completeness of recovery, 10 micrograms of iron were pipetted into a 25 ml. volumetric flask and reagents, starting with (1:1) nitric acid, added in the order given above. The reading obtained for the transmittancy of this solution--after correction for the blank--was then regarded as that which should be obtained for a similar quantity of iron "taken through" the proposed procedure, providing it is capable of completely separating and isolating such quantities of iron. In Table I are tabulated the readings observed when 10 micrograms of iron are analyzed for by the new method both in the presence and absence of a one milliliter aliquot of a pure synthetic Watts type plating bath. The readings are compared to the "theoretical" reading that should be duplicated if iron recovery is complete.

Table I

Comparison of Experimental to Theoretical Readings

Theoretical reading	33
Reading obtained with proposed method - no bath present	30
Reading obtained with proposed method - in presence of synthetic bath	31

The readings in Table I show that practically all of the iron added is separated and isolated by the proposed procedure even in the presence of the nickel bath aliquot.

Preparation of the Calibration Curve

Since the data in Table I indicates that iron in a pure nickel bath can be successfully determined by the proposed method, readings for the preparation of a calibration curve are now obtained by adding various quantities of a standard iron solution to a separatory funnel containing a 1 ml. aliquot of the pure synthetic Watts type nickel bath mentioned above and then following the recommended routine procedure given in detail near the end of the paper starting with step (2). The readings observed are tabulated in Table II.

Table II

Date Obtained for the Calibration Curve

Gamma Iron Present	Readings	Average Readings	Blank	Corr. Av. Readings	Mean Av. Reading
0	23-19-21	21			21
0	20-22-20	21			
0	17-20-12	19			
10	46-48-47	47	21	26	28
10	54-53-53	53	21	32	
10	49-47-47	48	21	27	
20	94-89-85	89	21	68	62
20	67-67-68	68	21	47	
20	94-95-91	93	21	72	
50	189-186-185	187	21	166	163
50	182-182-187	184	21	163	
50	182-176-179	179	21	158	
100	310-305-315	310	21	289	305
100	340-330-325	332	21	311)	
100	335-330-345	336	21	215	

By plotting the mean average readings against the corresponding amounts of iron, the curve shown in Fig. 2 is obtained. The resulting straight line shows that Bouguer-Beer's Law is obeyed by the iron-ortho-phenanthroline system over the concentration range tested.

A Klett-Summerson photoelectric colorimeter with their #54 green filter is used to get these readings. This filter is used because the wave length band at which it transmits the most light--about 525 millimicrons--is close to the band at which the iron-ortho-phenanthroline system shows the greatest amount of absorption--508 millimicrons. Fig. 1 shows the transmittancy curves for the filter and the colored system. A Beckman spectrophotometer was used in getting the data needed to prepare these curves. If one does not have a wave length selector on his instrument, he should always use a filter whose maximum transmission band corresponds as closely as possible to the wave length band most strongly absorbed by the colored system. In this way, it is possible to attain the greatest sensitivity for the colored system and if the filter's transmission drops off sharply on either side of this band, a minimum absorption due to other ions that may be present.

Determination of the Accuracy and Precision of Method

Having a calibration curve, the accuracy and precision of the proposed method can now be checked.

To determine the accuracy of the method under conditions similar to those that might be met in industrial work, small amounts of various metallic salts were dissolved in 100 ml. of pure Watts bath and the accuracy of the procedure determined in the presence of these impurities.

Table III shows the metallic ions and the quantity of each that were added to the bath.

These elements are added to the bath as the solid chlorides, sulfates or nitrates wherever possible. All the salts dissolve except the calcium. The solution is heated, shaken thoroughly and then cooled. It is then filtered to remove the insoluble calcium salts and the filtrate used for the accuracy and precision tests.

Table III

Kind and Quantity of Ions Added to the Plating Bath

Metal Ion Added	Quantity Added in Mgs.	Equivalent in grams/liter
Aluminum	100	1.0
Cadmium	100	1.0
Chromic oxide (CrO_3)	20	0.2
Copper	20	0.2
Lead	5	0.05
Manganese	100	1.0
Silicon	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

Employing exactly the same procedure as used to prepare the calibration curve, Table IV shows the results obtained in checking the accuracy attained on single runs.

Table IV

Data on Accuracy Test

Gamma Iron Added	Readings	Average Reading	Blank	Corrected Average Reading	Gamma Iron Recovered
10	56-56-57	56	21	35	11.0
20	84-88-80	84	21	63	20.0
50	182-178-179	179	21	158	52.0
70	246-305-305	245	21	224	74.0
100	288-305-305	299	21	278	92.0

The average accuracy of the method in the presence of the added impurities is about 6% when the procedure is closely followed.

An additional check on the accuracy obtainable by this method resulted from sending samples of a test solution and copies of the proposed method to several companies for check analyses. The organizations which kindly consented to test this method were the Bethlehem Steel Corporation, Bethlehem, Pa.; Foster D. Snell, Inc., Brooklyn, N.Y.; and the Bell Telephone Laboratory, New York, N.Y. The test solution was prepared by adding enough iron to 100 ml. of the impure bath used above to give it a concentration of 46.5 micrograms/ml. Their results and those obtained by the writers are shown in Table V.

Table V

Results Obtained by Various Laboratories Using Proposed Method

Laboratory	Micrograms/ml. of Iron
Bethlehem Steel Corp.	46.0
Foster D. Snell, Inc.	46.0
Bell Telephone Laboratories	47.5
Lehigh University	47.0

To test the precision of the method, six duplicates containing 50 gamma of iron were run. Results are shown in Table VI. Precision is only fair, but probably good enough for routine work. Results are generally somewhat high.

Table VI

Precision of Procedure

Gamma Iron Added	Readings	Average Reading	Blank	Corrected Average Reading	Gamma Iron Found
50	182-178-179	179	21	158	51.8
50	165-167-165	166	21	145	48.0
50	186-184-186	185	21	164	53.8
50	177-178-183	179	21	158	51.8
50	183-183-180	181	21	160	52.3
50	179-182-180	180	21	159	52.0

Recommended Routine Procedure

Reagents Required:

1) Cupferron solution 1%

Dissolve 0.25 grams of the reagent in 25 ml. of pure distilled water. Keep the solution cold at all times. Make it up fresh every day.

2) Amyl acetate . . . . c.p. grade

3) Nitric acid . . . .(1:1)

Dilute the concentrated acid with an equal volume of H_2O.

4) Hydroxylamine hydrochloride solution 10%

Dissolve 10 grams of the reagent in water and dilute to 100 ml.

5) O-phenanthroline solution 0.25%

Dissolve 0.25 grams of the reagent in 100 ml. of H_2O. To hasten solution, it would be advisable to warm the solution a little.

6) Sodium acetate buffer solution 20%

Dissolve 200 grams of hydrated sodium acetate in H_2O and dilute to one liter.

7) Synthetic Watts type nickel plating bath

330 grams $NiSO_4.7H_2O$, 45 grams $NiCl_2$, and 30 grams boric acid are dissolved in pure distilled water to make one liter of solution.

8) Standard iron solution . . . . . 1 ml. = 10 micrograms

Dissolve 702 milligrams of ferrous ammonium sulfate ($FeSO_4.(NH_4)_2SO_4.6H_2O$) in a liter of approximately 0.1 normal

HCl. Dilute 10 ml. of this stock solution to 100 ml. and mix thoroughly. 1 ml. = 10 gamma of iron.

Apparatus Required:

Separatory funnels - two Squibb type short-stemmed funnels of 60-100 ml. capacity.

Pipettes and burettes

25 ml. flask

Klett-Summerson colorimeter with green filter #54 or any other suitable photoelectric colorimeter or spectrophotometer.

Procedure:

For routine control work, the following procedure should give satisfactory results if closely followed:

Separation of the Iron

1) Pipette one ml. of the nickel plating bath into a separatory funnel.

2) Add 10 ml. of cold H_2O and then 1 ml. of cold 1% cupferron solution. Make certain that both the water and cupferron are cooled to at least 15°C. The lower, the better.

3) Shake for about 1 minute and then allow the solution to stand for 10 minutes. Do not shorten this standing period unless tests have shown that all the iron is precipitated by the cupferron in the shorter time interval.

4) Add 5 ml. of amyl acetate from a burette, shake for 30 seconds, allow liquid layers to separate, and draw off the bottom (aqueous) layer into another separatory funnel.

5) Repeat the extraction with another 5 ml. portion of amyl acetate. Draw off the aqueous layer and throw it away. All the iron has been removed by the amyl acetate.

Isolation of the Iron

6) Combine the amyl acetate extracts and wash them with 10 ml. of H_2O. Again throw the aqueous layer away.

7) Add 2 ml. of the (1:1) HNO_3 acid from a burette, shake hard for 2 minutes, and run the aqueous layer, after separation, into a 25 ml. flask.

8) Shake the amyl acetate layer with 5 ml. of H_2O for about 30 seconds and run the washings into the same flask. The amyl acetate at this point should be green in color. Discard.

Development of the Colored System

9) Now add in succession with mixing between additions 1 ml. of hydroxylamine hydrochloride, 2 ml. of the O-phenanthroline reagent and 15 ml. of sodium acetate solution to the flask. The last two reagents were dispensed from burettes and the first with a pipette.

10) If necessary, dilute to the mark with H_2O and mix well.

11) Using a testtube partially filled with water as the reference liquid, adjust the colorimeter so that the galvanometer pointer is at its zero position when the dial reading is zero. If the instrument used has a wave length selector, set it at 508 millimicrons.

12) Pour the water out of the testtube, rinse it out a couple of times with small portions of the test solution and then partially fill the tube with it.

13) Put the testtube back in the colorimeter and rotate the dial until the galvanometer reading returns to its zero position. Record the scale reading.

14) Run a blank following the above procedure except for the addition of the O-phenanthroline and record the scale reading. The blank was found to be fairly constant and need only be run from time to time.

15) Subtract the blank reading from the sample reading to get the correct measure of the light transmitted by the solution. It must be emphasized that this method of correcting for the blank is permissible <u>only</u> when the scale readings of the instrument give the extinction of the solution directly or is related to the extinction--i.e., when the scale is a logarithmic one.

16) The corrected scale reading is looked up on the calibration curve and the amount of iron corresponding to it is the quantity of iron in the volume of the bath originally taken for analysis.

Calculations

Calculation of the amount of iron present in grams/liter.

Suppose a corrected reading of 158 is obtained when a one ml. aliquot of the plating bath is used. The corresponding quantity of iron according to the calibration curve is 50.2 gamma of iron.

Hence, in 1 ml. of the original solution, there are 50.2 gamma or 0.0502 milligrams of iron. Therefore, in a liter of the bath there will be 0.0502 x 1000 = 50.2 mgs./l. of iron or about .05 grams/l. of iron.

As explained in the previous paper on the determination of lead in nickel plating baths, if a solution is known to transmit light in accordance with Bouguer-Beer's Law, it is possible to eliminate the need for a calibration curve if the instrument has a logarithmic scale as does the Klett-Summerson colorimeter used in this investigation.

Run an unknown, a standard sample, and a blank treating each exactly the same. Observe their scale readings and correct the unknown and standard sample for the blank as described above. Since the readings for both the standard and the unknown are directly proportional to their concentrations--if Bouguer-Beer's Law holds--the concentration of the unknown is calculated by using the following formula:

$$\frac{\text{Concentration of Standard}}{\text{Corrected Scale Reading of Standard}} \times \text{Corrected Reading of Unknown} = \text{Concentration of Unknown}$$

Once the standard is run, it is not necessary to run it with each unknown although it would be desirable since

$$\frac{\text{Concentration of Standard}}{\text{Corrected Scale Reading of Standard}}$$

is a constant. It would only be necessary to multiply the corrected scale reading of the unknown by this constant factor to get the concentration of iron in the unknown.

Discussion Regarding the Procedure

Cupferron is usually used at a temperature of 6°C. and if means are at hand, the solution and the water should be cooled to this temperature. Small amounts of iron are not completely precipitated by the cupferron from a bath containing none or only small quantities of other impurities if the H_2O and the cupferron are at room temperatures--about 25-28°C. When impurities in the bath are present in the amounts used in testing the accuracy and precision, this cooling is not necessary as one of the impurities--probably the copper--partially co-precipitates with the iron and assists in its complete precipitation. The addition of an element that can coprecipitate with one present in trace quantities is a common way to get complete precipitation of the trace element. However, since one will usually not know exactly how much of or what metallic ions will be present in the bath, it seems best not to take a chance on some other element coprecipitating with iron to get complete precipitation but to cool the solutions before use.

Tests indicate that it takes appreciable time for the precipitation of iron to be complete even when cold solutions are used and a "collector" is present. Ten minutes has been found to give good results. The standing period may be shortened, but one must always be certain that complete precipitation will take place in the time interval taken. This is one of the critical points of this analysis.

The p^H of the solution at which the precipitation of iron with cupferron takes place must be watched. If the acidity is too low, other elements may be precipitated too. If too high, not all the iron may come down. In this study, the solution at the time the cupferron is added had a pH = 2.5. If the acidity is much higher than this value, it should be cut down to within this range.

"Stop and Go" Method for Iron

For those desiring only an approximation of the amount of iron in a nickel plating bath, the procedure below is recommended.

The method is based on the yellow to brown color resulting from the solution of the iron cupferride in amyl acetate. The color of the solution is matched against a set of permanent standards each of which represents a definite quantity of iron. The sample then contains an amount of iron equal to that represented by the standard it most nearly matches in color.

The permanent standards are prepared from the following solutions:

a) potassium dichromate - 5.0 mgs. of chromium/ml.

b) cobalt chloride - 59.59 grams of $CoCl_2.CH_2O$/liter in 1% HCl.

c) ferric chloride - 45.05 grams of $FeCl_3.6H_2O$/liter in 1% HCl.

The quantities of each solution used are so chosen that their resulting colors appear to be the same as those produced by solutions of 10, 30, 50, 80, and 100 micrograms of iron dissolved in 5 ml. of amyl acetate as iron cupferride. The quantities required are given in Table VII.

Table VII

Preparation of the Permanent Standards

Iron equivalent - in micrograms:	10	30	50	80	100
Ml. of $K_2Cr_2O_7$ solution	2.5	---	---	---	---
Ml. of $FeCl_3.6H_2O$ solution	---	11.2	18.6	28.5	35.7
Ml. of $CoCl_2.6H_2O$ solution	1.2	2.3	3.8	5.6	9.1
Ml. of H_2O	74	20	15	---	---

Recommended Procedure:

1) Follow the recommended routine procedure given for the accurate determination of iron up to and including step (4).

2) Wash the amyl acetate twice with 5 ml. portions of H_2O.

3) Run the amyl acetate solution into a small Nessler or testtube.

4) Compare the color of the unknown with the colors of a set of permanent standards prepared as indicated in Table VII. Five ml. of each solution is put into a tube of the same size and shape as that containing the unknown. The comparison is best made by viewing the tubes laterally against a white background under a fluorescent light if one is available.

5) Find the standard which most nearly has the same color as the sample. The amount of iron represented by this standard is then approximately the amount of iron in the sample.

The method--if properly followed--should give an accuracy of about 0.015 to 0.020 grams/l. of iron over the range tested.

Keep the standards in tubes that are tightly stoppered. They will last over a year if properly sealed. By this time, an operator will most likely be able to estimate the iron content of samples without reference to the standards.

Applicability of the Method to Other Types of Nickel Plating Baths

The procedure has been tested on chloride, 50-50, and high sulfate nickel plating baths and found to give satisfactory results.

Summary

Iron is separated from the other metallic ions present by precipitation with cupferron. The iron cupferride is extracted with amyl acetate and then returned to the aqueous solution by shaking the amyl acetate extract with (1:1) HNO_3. The iron is then reduced with $NH_2OH.HCl$, O-phenanthroline added, and the pH adjusted with sodium acetate. The light transmission of the ferrous O-phenanthroline complex is then measured using a Klett-Summerson colorimeter.

FIGURE (1)

(a) Extinction versus wave length for the ferrous iron-O-phenanthroline complex. The concentration is 50 ppm. of iron.

(b) Extinction versus wave length for Klett-Summerson filter #54. The extinction units on the right side of the figure apply to this curve.

Figure 1

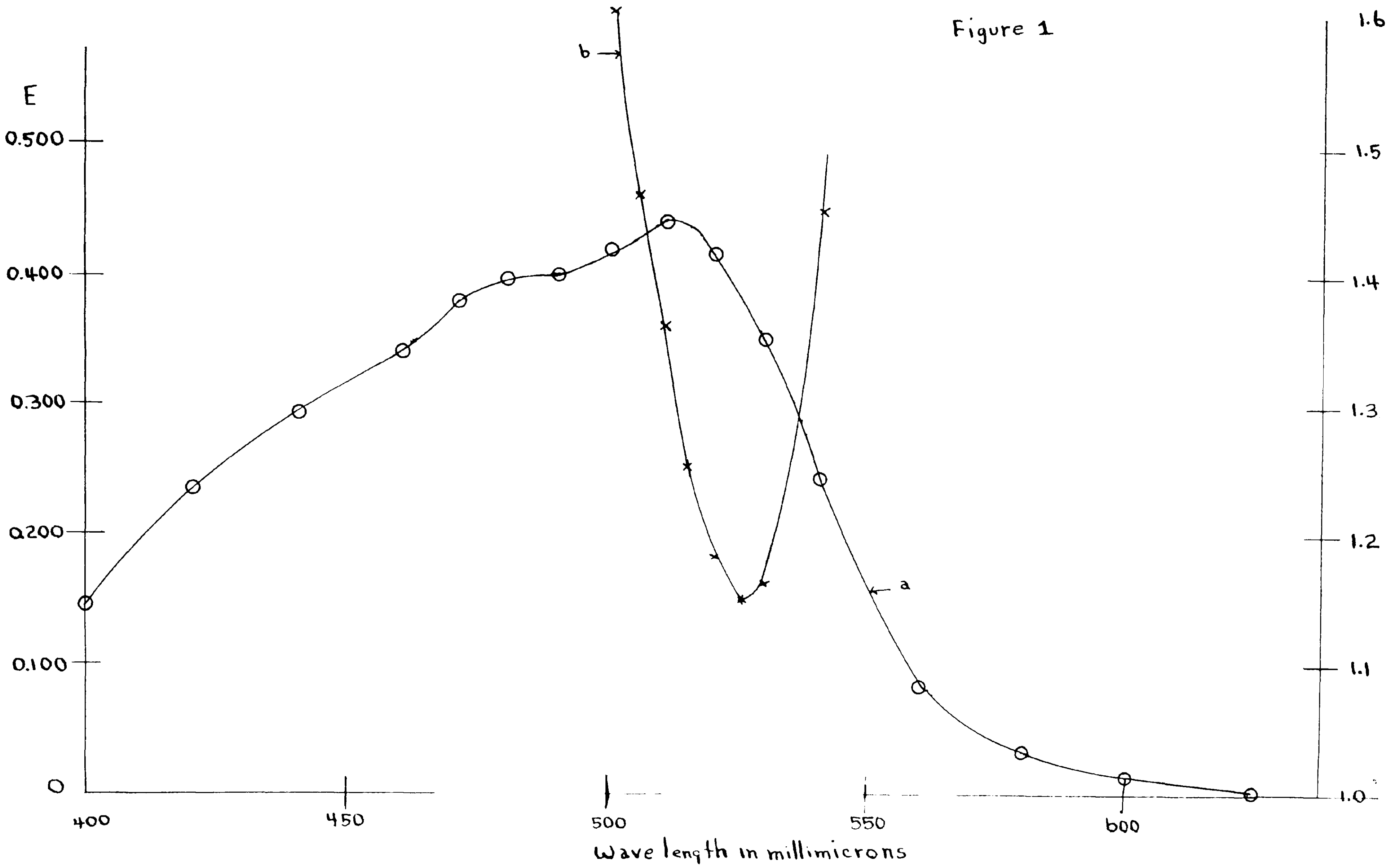

E
0.500
0.400
0.300
0.200
0.100
0
E
1.6
1.5
1.4
1.3
1.2
1.1
1.0
b
a
400
450
500
550
600
Wave length in millimicrons

FIGURE (2)

Calibration curve for the determination of iron in a Watts type nickel plating bath using O-phenanthroline.

Instrument used -- Klett-Summerson colorimeter with green filter # 54.

Type cell -- testtube.

Final Volume of Solution -- 25 ml.

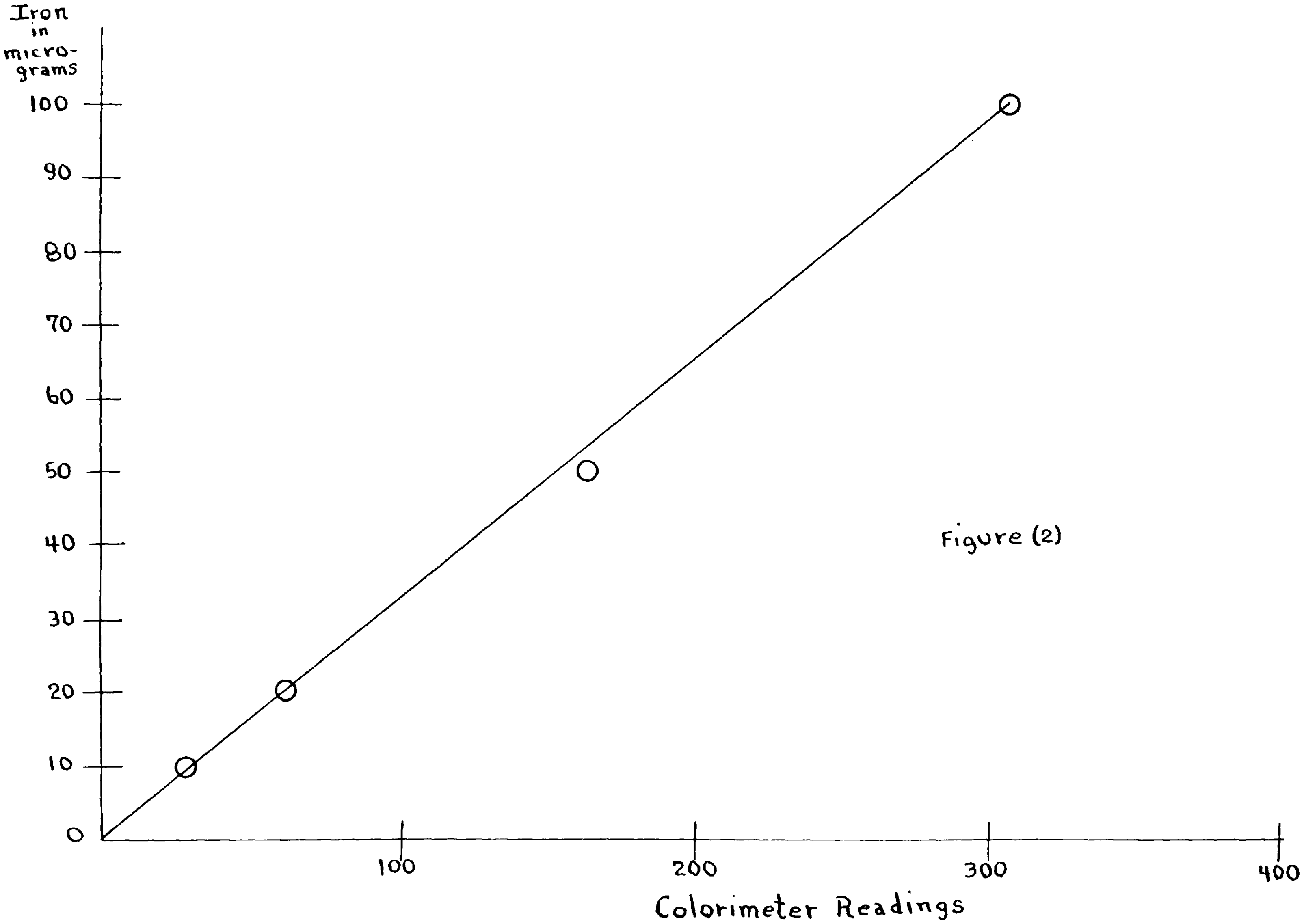

Iron in micro-grams
100
90
80
70
60
50
40
30
20
10
0
100
200
300
400
Colorimeter Readings

Figure (2)

SECTION C

THE DETERMINATION OF MANGANESE IN NICKEL PLATING BATHS

THE DETERMINATION OF MANGANESE IN NICKEL PLATING BATHS

The colorimetric determination of manganese by oxidation to permanganate in acid solution is so sensitive, specific, and simple in procedure that it should be readily applicable to the determination of manganese in nickel plating baths which may also contain appreciable quantities of aluminum, cadmium, chromic oxide (CrO_3), iron, lead, zinc, and calcium.

Other colorimetric methods have been used, but none has had the success of the permanganate method. With manganic compounds, a yellow color is developed with O-tolidine in the absence of chlorine (40). Manganates react with benzidine to produce a brilliant blue-green color. This is a very sensitive reaction (18, 121, 128). However, the color is given by other oxidizing agents and is not very stable. Manganese reacts with tetramethyldiaminodiphenylmethane to give a deep blue to violet colored solution (49, 50, 126). Again, any strong oxidizing agent will give the same reaction with the reagent. Another quantitative method for manganese is based on the reaction of formaldoxime with manganous ions (113). A brown-red color is formed.

To oxidize the manganese to permanganate in acid solution, various oxidizing agents have been used. Lead dioxide and sodium bismuthate were satisfactory, but the excess reagent had to be removed by filtration. Ammonium persulfate plus silver as a catalyst is widely used, but a true permanganate color is not always obtained, and it is difficult to tell when oxidation is complete. The best oxidizing agent appears to be sodium or potassium periodate. It oxidized the manganese and then the excess periodate stabilizes the color for months if kept in the dark (79, 92, 129).

Manganese is oxidized according to the equation:

$$2MnSO_4 + 5KIO_4 + 3H_2O \rightarrow 2HMnO_4 + 5KIO_3 + 2H_2SO_4.$$

The oxidation is carried out in strong acid solutions containing nitric, sulfuric, phosphoric, or perchloric acid. Usually mixtures are used. If much iron is present, sulfuric acid, or phosphoric acid must be present to prevent the precipitation of ferric periodate. Phosphoric acid decolorized the ferric iron and also prevents the possible precipitation of periodates or iodates of manganese (104). Sulfuric acid can be replaced by equivalent amounts of perchloric acid. For information on the effect of acidity and acids on the oxidation, the reader is referred to papers by Williard and Greathouse (129) and Richards (92).

Most impurities, with a few exceptions, do not interfere except when they are colored. The effect of copper, nickel, and chromate ions can be compensated for by using a blank containing similar amounts of these metals. Silver, lead, and mercury will give no precipitates if enough acid is present, but bismuth and tin will give precipitates even in very strong acid solutions (80, 104).

Developmental Work

Since the conditions under which manganese is quantitatively oxidized to permanganate by alkali periodates are so well known, little trouble was anticipated in applying the reaction to the determination of manganese in plating baths.

Only two points seemed to warrant some preliminary investigation:

1) The destruction of organic matter in plating baths and the removal of chlorides and reducing agents which react with permanganate.

2) As the method desired is to be applicable in the presence of appreciable quantities of the trace elements mentioned previously, how would they affect the development of the permanganate color?

The first problem was easily solved by adding a mixture of nitric and perchloric acids to an aliquot of the bath and heating to fumes of the latter.

Of the ions to be present in the bath, only copper, chromate, and nickel ions can possibly interfere, and their presence can be compensated for by running a blank and properly selecting the wave length of the incident light.

Preparation of the Calibration Curve

Having eliminated all apparent difficulties, a procedure based on preliminary tests and methods recommended by other investigators (92, 104, 129) was worked out.

In order to check the accuracy and precision obtainable by this method, a calibration curve is prepared covering the range of 0 to 1000 micrograms of manganese. This is done by pipetting 0.5, 1, 2, 5, and 10 ml. quantities of a standard manganese solution respectively into five 200 ml. flasks containing 10 ml. of a pure synthetic Watts type plating bath. A sixth flask containing a similar portion of the bath serves as the blank. The recommended routine procedure given near the end of the paper is now followed, beginning with step (2), to develop the permanganate color.

The colorimeter readings obtained using a Klett-Summerson colorimeter with their #54 green filter are tabulated in Table I.

Table I

Calibration Curve Data

Gamma Manganese	Readings	Average Reading	Blank	Corrected Average Reading	Mean Average Reading
0	27-20-22	23			23
0	23-24-21	23			
50	35-36-36	36	23	13	
50	34-36-34	35	23	12	12
50	30-33-31	32	23	9	
100	44-44-45	44	23	21	
100	46-48-43	46	23	23	22
100	44-45-42	44	23	21	
200	69-67-67	68	23	45	
200	68-68-68-	68	23	45	45
200	66-68-67	67	23	44	

Table I (Cont'd)

Gamma Manganese	Readings	Average Reading	Blank	Corrected Average Reading	Mean Average Reading
500	134-137-137	136	23	113	112
500	139-141-134	138	23	115	
500	133-128-133	131	23	108	
1000	258-252-248	253	23	230	226
1000	242-250-243	245	23	222	
1000	253-252-242	249	23	226	

The calibration curve prepared by plotting the mean average readings against the corresponding amounts of manganese is shown in Figure 1. The straight line obtained shows that Bouguer-Beer's Law is obeyed by the permanganate solution at least over the concentration range tested. It is supposed to hold for concentrations up to 150 milligrams/liter.

To obtain maximum sensitivity in determining manganese by this method, the incident light should have a wave length of about 525 millimicrons because transmittancy curves such as the one shown in Figure 1 for permanganate solutions exhibit maximum absorption at this wave length. Therefore, when a filter photometer is used, the maximum transmittancy of the filter should be for light of about this wave length. Figure 2 also shows the transmittancy curve for the green filter used in this investigation. It exhibits maximum transmission between 525 and 540 millimicrons and hence is satisfactory for this work.

Determination of the Accuracy and Precision of the Method

To check the possible accuracy of the method under conditions similar to those which are likely to be met in industrial practice, small amounts of various metallic salts were dissolved in 100 ml. of the pure nickel plating bath and this solution used in testing accuracy and precision instead of the pure bath used in preparing the calibration curve.

Table II shows the metallic ions and the amounts added. These metals and compounds are added to the bath as the solid chlorides, sulfates or nitrates, if possible. All the salts added dissolve except the calcium. The solution is heated, shaken thoroughly, allowed to cool, and then filtered.

Table II

Kind and Quantity of the Ions Added to the Bath

Metal Ions	Amount Added	Equivalent in grams/1.
Aluminum	100	1.0
Cadmium	100	1.0
Chromic oxide	20	0.2
Copper	20	0.2
Iron	100	1.0
Lead	5	0.05
Silicon	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

The procedure is the same as that used in the preparation of the calibration curve. Table III shows the results obtained on single runs.

Table III

Results of the Accuracy Tests

Gamma Manganese Added	Readings	Average Readings	Blank	Corrected Average Readings	Gamma Manganese Recovered
0	29-27-28	28	28		
50	37-38-39	38	28	10	43.0
200	75-75-72	74	28	46	200
300	97-96-94	96	28	68	310
500	146-145-143	145	28	117	520
700	195-190-187-191	191	28	163	720
1000	260-262-258	260	28	232	1020

Except for the sample containing 50 gamma of manganese, the accuracy is better than 10%. It will be noted that the results are somewhat high. Note, too, that although the amount of nickel present in this test is the same as that used in preparing the calibration curve, there is a difference of 5 scale divisions in the blanks. This was probably due to the presence of the small amounts of copper, iron and chromate added.

To get an additional check on the accuracy of the proposed procedure, a quantity of a standard solution of manganese was added to the synthetic bath used in the above accuracy tests so that each milliliter of the bath contained

50 micrograms of manganese.

Portions of this solution were sent to three laboratories who kindly consented to check the recommended procedure. They were the Research Laboratory of the International Nickel Company, Inc., Bayonne, N.J.; Foster D. Snell, Inc. of Brooklyn, N.Y.; and the Bethlehem Steel Corporation, Bethlehem, Pa.

The results obtained by these laboratories and the writers on this sample are shown in Table IV.

Table IV

Results of Check Analyses

Laboratory	Milligrams/l. Manganese Reported
A	56.0
B	55.0
C	49.5
D	55.0

In testing precision, four duplicate runs were made containing 500 gamma of manganese using the same procedure as followed in preparing the calibration curve. Results are shown in Table V.

Table V

Precision Data

Gamma Manganese Added	Readings	Average Readings	Blank	Corrected Average Reading	Gamma Manganese Found
500	147-147-142	145	28	117	520
500	149-140-141	143	28	115	510
500	147-139-143	143	28	115	510
500	146-145-143	145	28	117	520

The results show that the method has good precision.

Recommended Routine Procedure

The procedure finally adopted for the determination of manganese in nickel plating baths is the following:

Solutions Required:

1) Concentrated acids . . . . c.p. grade

Perchloric (70 to 72%), nitric (sp. gr. 1.42), phosphoric (95%).

2) Sodium periodate (solid) . . . . c.p. grade

3) Sodium bisulfite solution 30%

Add about 3 grams of the salt ($NaHSO_3$) to 10 ml. of H_2O and shake thoroughly. This amount will just about saturate the solution.

4) Standard manganese solution . . . . 100 micrograms/ml.

Dissolve 288 milligrams of purest reagent grade potassium permanganate in 100 ml. of 2% (by volume) sulfuric acid. Add sodium bisulfite dropwise until the solution becomes colorless. The solution is now diluted to one liter and mixed well. Each milliliter contains 100 gamma of manganese.

5) Watts type nickel plating bath

330 grams $NiSO_4.7H_2O$, 45 grams $NiCl_2.6H_2O$ and 30 grams of boric acid are dissolved in pure distilled water to make one liter of solution. The nickel salt should be of A.C.S. Analytical Reagent quality.

Apparatus Required:

10 ml. pipette - accurately calibrated

3 - 50 ml. burettes

200 ml. Erlenmeyer flasks

Small glass spoon

Klett-Summerson colorimeter with #54 filter or any other type of photoelectric colorimeter of spectrophotometer. Any filter showing maximum transmittancy around a wave length band of 525-550 millimicrons can be used.

Oxidation of Reducing Agents

1) Place 10 ml. of the plating bath into a 200 ml. Erlenmeyer flask.

2) Add 10 ml. of nitric acid until crystals separate then add 15 ml. $HClO_4$ and heat until fumes are copiously evolved.

Development of the Colored System

3) Cool. Dilute to 70 ml. with distilled water and when all the salts are redissolved, add 5 ml. of phosphoric acid.

4) Add approximately 0.4 gram of solid sodium periodate using the little glass spoon, heat almost to boiling and

digest at this temperature for about 10 minutes.

5) Cool, transfer the solution to a 100 ml. volumetric flask, dilute to the mark with distilled water, and shake thoroughly to mix.

Measuring the Transmittancy of the Unknown

6) Using a clean testtube cell partially filled with distilled water as the reference liquid, adjust the colorimeter so that the galvanometer pointer is at the zero position when the dial reading is zero.

7) Pour out the water, rinse the testtube a couple of times with small portions of the test solution in the flask, and then partially fill the testtube with the sample. Replace the testtube in the colorimeter and rotate the dial until the galvanometer pointer returns to its original position. Record the scale reading.

8) Run a blank following the same procedure except for the addition of the periodate and correct for same as described below under "Calculations".

9) From the calibration curve, the quantity of manganese corresponding to the corrected scale reading of the test sample is noted and the amount of manganese in the bath calculated.

Calculations

Suppose the scale reading using 10 ml. of the bath for a sample is 191. Also, the blank reading is 28. Therefore, 191 - 28 = 163, the corrected scale reading of the sample. From the calibration curve, a reading of 163 corresponds to

0.71 mg. of manganese. There is then 0.71 mg. of manganese in 10 ml. of the bath. Hence 0.71 x 100 = 71 mg. manganese/ liter (71 ppm) or 0.071 grams/l. is the concentration of manganese in the plating bath.

If a solution is known to transmit light in accordance with Bouguer-Beer's Law, it is possible to eliminate the need for calibration curves if the instrument used has a logarithmic scale. Run an unknown, standard, and blank. Correct the unknown and standard for the blank as described. Since the readings for both the standard and the unknown are directly proportional to the concentration of manganese, the concentration of manganese in the unknown is calculated by using the formula:

$$\frac{\text{Concentration of standard}}{\text{Corrected standard reading}} \times \text{Corrected unknown reading} = \text{concentration of unknown}$$

Discussion

Reducing substances and chlorides that can react with periodate or permanganate must be destroyed or driven off. Hence, the first step is to oxidize all the reducing agents present. In this procedure, the oxidation is accomplished by adding a mixture of nitric acid and perchloric acid to the sample and boiling until fumes of the latter are evolved. This treatment will oxidize any reducing agents such as ferrous iron, sulfites, nitrites and volatilize chlorides.

"Stop and Go" Method for Manganese

In this procedure, the method of oxidation and development of the permanganate is the same as that given in the above recommended routine procedure. A blank and unknown are carried through the same procedure, transferred to Nessler tubes and then small portions of a standard potassium permanganate solution added until the solutions in the two tubes match in color. The detailed procedure is as follows:

Oxidation of the Sample and Development of the Colored System

1) Pipette two aliquots of the bath into separate 200 ml. Erlenmeyer flasks. One will serve as a blank.

2) Starting with step (2) of the Recommended Routine Procedure proceed in the same way up to and including step (4) except that no sodium periodate is added to the blank.

3) Cool the solutions and transfer them to 100 ml. Nessler tubes.

Comparison of the Colors

4) Dilute the unknown to the 100 ml. mark, and the blank to about 95 ml. Shake.

5) Now add 1 ml. of the potassium permanganate solution to the blank, shake well and compare the color of the solution in the blank with the color of the sample viewing them horizontally against a white background.

6) Continue adding portions of the permanganate solution to the blank, until the colors in the two tubes match. The amount of manganese is then determined from the volume of potassium permanganate required to match the color of the sample.

a) Suppose 6.5 ml. are required. Since each ml. is equal to 100 micrograms of manganese, then there are 6.5 x 100 = 650 micrograms or .65 mg. of manganese in the 10 ml. of nickel plating bath taken for analysis.

.65 x100 = 65 mg./l. or .065 grams of manganese/l. of bath.

7) The method is accurate to at least 50 gamma.

8) The following chart of color changes may be used as a rough guide if one does not care to run a blank.

Color of Sample	Micrograms of Manganese	
green	0	
blue-green	100	solution becomes bluer
blue-green	200	
gray-blue	300	
gray-blue	400	
purplish-blue	500	solution gradually becomes more purple
purplish-blue	600	
purplish-blue	700	
blue-purple	800	blue shade disappears gradually
blue-purple	900	
blue-purple	1000	

Applicability of the Method to Other Types of Plating Baths

The method was tested on chloride, 50-50, and high sulfate baths as well as on the Watts type bath and found to give satisfactory results.

Summary

The manganese is oxidized by sodium periodate in an acid mixture of phosphoric and perchloric acids to permanganate. The transmission of the solution is then measured using a Klett-Summerson Colorimeter with green filter # 54.

FIGURE (1)

Calibration curve for the determination of manganese in a Watts type nickel plating bath by oxidation with sodium periodate.

A Klett-Summerson colorimeter with green filter #54 was used.

Type of cell -- testtube.

Final Volume of Solution -- 100 ml.

Figure (1)

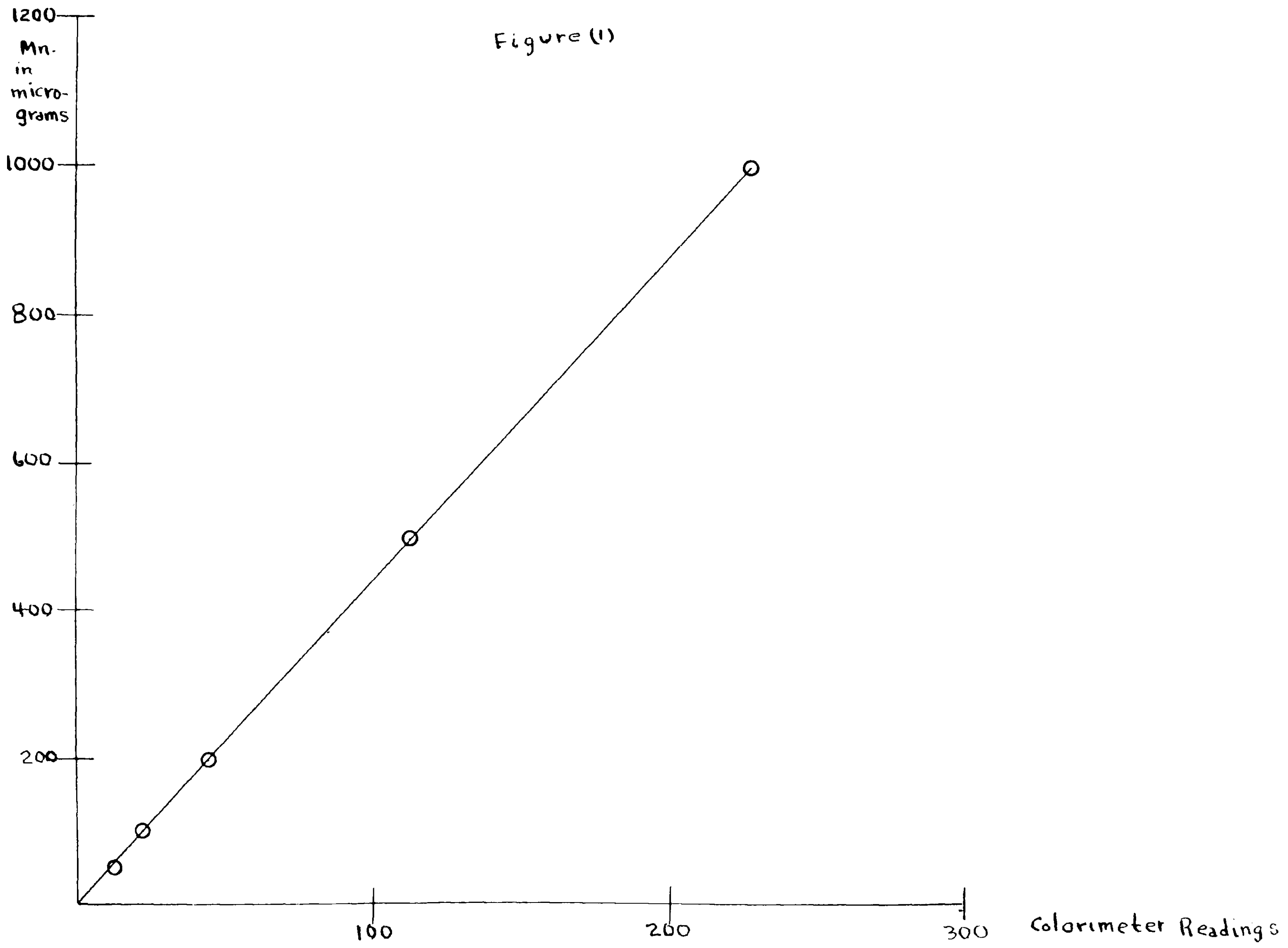

1200
Mn. in micro-grams
1000
800
600
400
200
100
200
300
Colorimeter Readings

FIGURE (2)

Curve (a) --- Extinction versus wave length of sodium permanganate -- 50 micrograms of manganese in 100 ml.

Curve (b) --- Extinction versus wave length for the Klett-Summerson filter #54. The extinction units on the right apply to this curve.

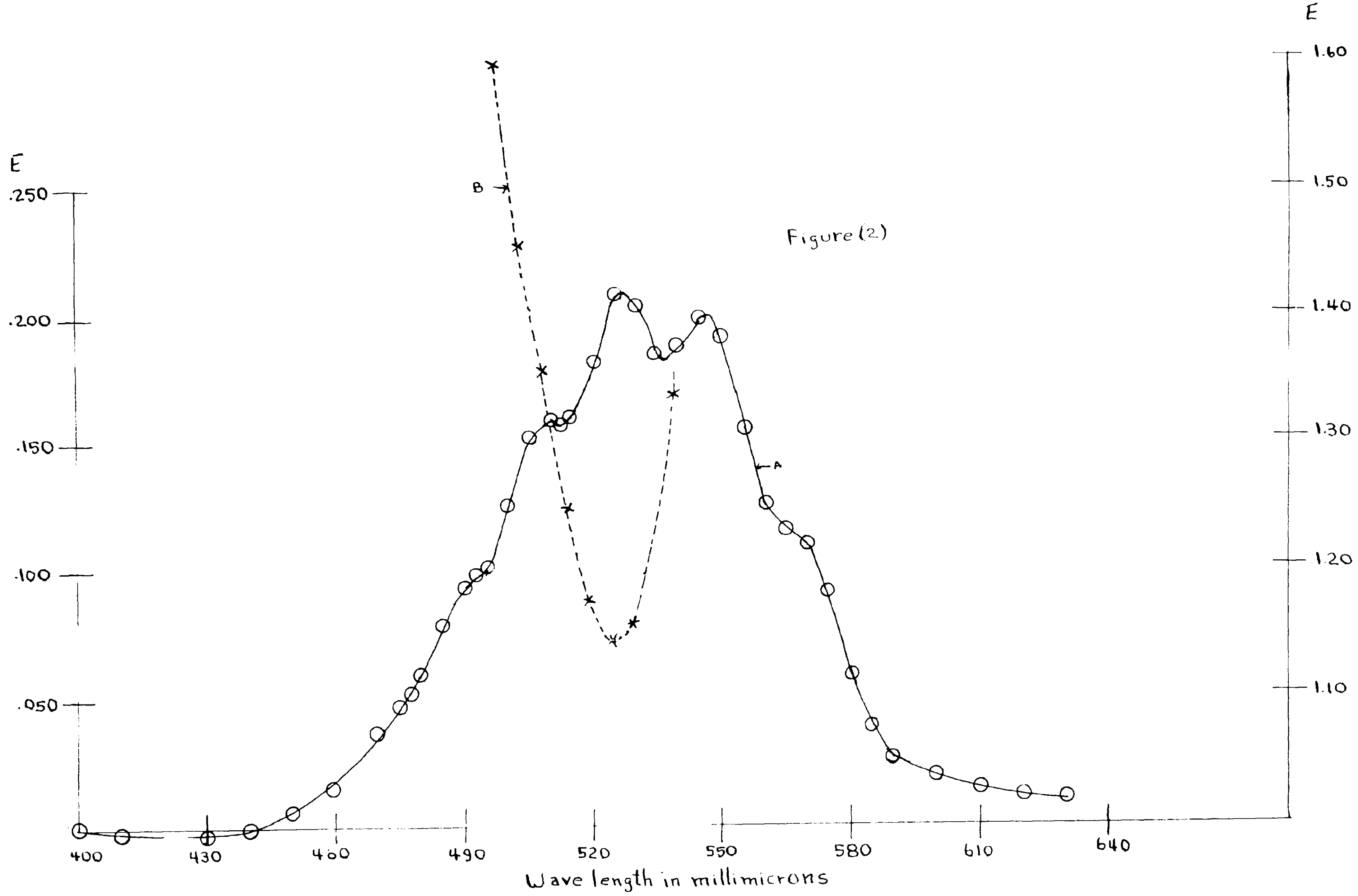


Figure (2)
E
.250
.200
.150
.100
.050
E
1.60
1.50
1.40
1.30
1.20
1.10
B
A
400
430
460
490
520
550
580
610
640
Wave length in millimicrons

SECTION D

THE DETERMINATION OF COPPER IN NICKEL PLATING BATHS

THE DETERMINATION OF TRACES OF COPPER IN NICKEL PLATING BATHS

Introduction

The purpose of this investigation was to develop an analytical procedure for the determination of very small amounts of copper in nickel plating baths. As in previous articles in this series, the method desired was one that would be applicable in the presence of appreciable quantities of other ions--namely chromate, silicate, calcium, aluminum, cadmium, lead, iron (ferric or ferrous), and manganese.

A literature search showed that little work has been done in the past on this subject. Several electrolytic methods have been reported. Pinner, Soderberg, and Baker (90) determined copper in nickel baths this way. Hills (53) determined copper in cadmium cyanide baths by taking an aliquot of the bath down to fumes of H_2SO_4, adding HNO_3 and plating out the copper. Harris (48) determined copper in chromium plating baths by precipitating copper as CuS, dissolving the sulfide in HNO_3 and plating out the copper. Thompson and Thomas (123), working on nickel salts to be used in plating baths, also analyzed for copper by electrodeposition. Knapp (67) separated and determined copper in a nickel plating bath by means of dithizone.

As a colorimetric method was desired, a further search of the chemical literature was made for references pertaining to the usual means employed in separating very small quantities of copper from other constituents in a solution and for colorimetric procedures that have been developed for copper analysis.

Reliable and quantitative methods for the isolation of traces of copper are not too numerous. Precipitation with hydrogen sulfide is apparently satisfactory if the mixture is allowed to stand overnight before filtration (2, 23, 46). Sodium diethyl dithiocarbamate ($N(C_2H_5)_2CS_2Na$) will also precipitate small quantities of copper. The resulting compound can be isolated by extracting it with amyl alcohol, amyl acetate, carbon tetrachloride or bromobenzene (26). Dithizone will extract traces of copper from a slightly acid solution. Electrolytic deposition of the copper is another way to isolate it (4 7). An interesting method has also been described by Clarke and Hermance (19). Filter paper is impregnated with cadmium sulfide and the solution containing the copper filtered through the paper. The copper reacts to form copper sulfide which remains on the paper while cadmium does into solution.

These methods of isolating small amounts of copper do not comprise all the methods that may give quantitative separations, but those that are known to give good results with micrograms of copper.

There are many reactions that have been used as a basis for the colorimetric determination of copper. It would be pointless to discuss all of them here. Hence, only a brief summary of the most popular methods will be given.

In the "carbamate" method, the copper is precipitated as copper diethyl dithiocarbamate. If precipitated in the presence of gum arabic, a golden brown suspension is obtained whose transmittancy is proportional to the copper concentration. If the colloid is omitted, the precipitate formed can be extracted by organic solvents such as those mentioned above and the solution used for the analysis (13, 26, 56).

In the dithizone method (6, 72, 83, 105), copper is extracted from a solution whose acidity is about 0.05 to 0.1 normal with an accurately measured quantity of dithizone solution and the transmittancy of the copper dithizonate or the excess dithizone measured.

For moderate amounts of copper, the ammonia method is widely used although any other ions that form colored complex ions with copper must be absent (118, 137). The solution is made ammoniacal and the intensity of the deep blue solution is a measure of the amount of copper present.

When potassium ferrocyanide (137) is added to solutions containing copper ions, a purplish brown color due to the complex salt $Cu_2Fe(CN)_6$ is formed. The intensity of this color is a measure of the quantity of copper present.

For the numerous other methods, the reader is referred to texts of Sandell (105), Yoe (137), Snell and Snell (118), and Mellan (81).

Developmental Work

To decide which reaction to utilize in analyzing for copper in nickel baths was quite a problem. In the "carbamate" method, nickel is also precipitated by the reagent. It is also extracted by the same solvents. Nickel could be removed before the addition of "carbamate" by precipitation with dimethyl glyoxime, but some copper might be lost as a result of absorption by the precipitate.

The dithizone method seemed satisfactory as none of the other elements that react with dithizone in acid solution--namely, palladium, gold, silver, mercury and bismuth were to be present in this investigation. Hence, the copper could be extracted with dithizone solution and the transmittancy of the extract measured as outlined above. However, in attempting to use the method, a number of difficulties were encountered. The calibration curve obtained with a colorimeter was curved and did not go through the origin. The point from which the curve started was dependent on the concentration of the dithizone originally used. Considering the possible range of copper in plating baths and the instability of dithizone solution, the method was given no further consideration.

Since the other methods commonly used for the analysis of copper did not appear to offer any more hope of being applicable to the problem than those already discussed, a search for a new method was made.

A reaction that seemed of interest is that between copper ions and 2-mercaptobenzothiazole

According to Spacu and Kuras (120), only copper will react with the reagent in an acetic acid solution to form an orange-yellow precipitate. Lead, bismuth, mercury, silver, gold, cadmium, and thallium will all form precipitates with the reagent in ammoniacal solution. As the reagent, in slightly acid solution, seemed to be almost specific for copper, its use was investigated further. Although Spacu and Kuras used the reagent in precipitating comparatively large quantities of copper, tests indicated that the reagent could definitely precipitate about 50 micrograms of copper in a volume of 25 ml.

Further, the copper mercaptobenzothiazole precipitate is soluble in amyl acetate forming a light yellow solution. Therefore, by precipitating copper with the reagent and extracting the precipitate with amyl acetate, copper can be isolated from the other constituents in the bath.

Since the color intensity of the amyl acetate extract did not vary enough with the copper concentration, it could not be used directly to determine copper. Hence, an attempt was made to develop the copper "carbamate" color in the amyl acetate solution since copper diethyl dithiocarbamate is also soluble in amyl acetate. After many trials, it was found that by adding dibutyl amine and carbon disulfide to the amyl acetate solution, a yellow brown solution was obtained whose intensity did vary considerably with the amount of copper present.

Effect of pH on the Precipitation of Copper

With a tentative procedure established, a study was made to determine the optimum pH at which to precipitate the copper with 2-mercaptobenzothiazole. Table I shows the relation between the pH of the solution when the reagent is added and the readings obtained with 100 micrograms of copper present.

Table I

Effect of pH on the Precipitation of Copper

pH	1.4	2.1	2.6	3.8
Colorimeter Readings	31.0	297	367	368

These results indicate that the final pH of the solution from which the copper is precipitated should be 2.6 or higher.

Preparation of the Calibration Curve

To prepare a working curve for the determination of copper by the procedure developed, 5 ml. portions of a pure Watts type nickel plating bath are pipetted into each of four 60 ml.

separatory funnels. Then 10, 30, 60, and 100 micrograms of copper are added successively to the funnels using the standard copper solution described below. The color in these solutions is then developed by following the recommended routine procedure given near the end of this paper.

The data obtained is tabulated in Table II.

Table II

Calibration Curve Data

Micrograms of Copper	Readings	Average Reading	Blank	Corrected Average Reading	Mean Average Reading
10	92-92-91	92	46	46)	45
10	89-88-90	89	46	43)	
30	175-174-173	174	46	128)	127
30	172-173-170	172	51	121)	
30	184-185-184	184	51	133)	
60	276-272-272	273	38	235)	237
60	290-290-294	291	46	245)	
60	270-266-270	268	38	230)	
100	440-435-445	440	46	394)	392
100	425-425-425	425	38	387)	
100	440-430-435	435	38	397)	

The calibration curve is then obtained by plotting the mean average readings in Table II against their corresponding concentrations of copper with the former as the abscissa.

A straight line is obtained--Figure 1--indicating that Bouguer-Beer's Law is followed by the colored system over the concentration range tested.

A blue filter, Klett-Summerson #42, is used in getting the data given in Table II because the transmittancy curve of the colored system (Figure 2) shows that its absorption is a maximum when the wave length of the incident light is about 435-440 millimicrons. Figure 2 also shows the transmittancy curve of the blue filter. It transmits a relatively narrow band of light which is a maximum for light of about 420 millimicrons. Hence, it is a good filter for the colored system under consideration since it shows maximum transmission for light of nearly the same wave length for which the colored system shows maximum absorption. This means maximum sensitivity, i.e., scale divisions per microgram of copper, and minimum interference due to absorption of light by other substances in the solution. Beckman spectrophotometer was used in getting the data for preparing the transmittancy curves.

If an instrument possessing a wave length selector is available for the work, the selector should be set at 435 millimicrons.

Accuracy and Precision Obtained with Proposed Procedure

To determine the accuracy obtainable with this method under conditions similar to those that may be met in operating plating baths, small amounts of various metallic salts are dissolved in 100 ml. of the pure synthetic Watts type bath whose composition is described below. The accuracy the procedure will give is determined in the presence of these "impurities". Table III shows the metallic ions and the quantity of each that is added to the bath.

Table III

Kind and Quantity of Ions Added to the Bath

Ion	Quantity Added in Milligrams	Quantity Expressed in gms./l.
Aluminum	100	1.0
Cadmium	100	1.0
Chromic oxide (CrO_3)	20	0.2
Copper	20	0.2
Lead	5	0.05
Manganese	100	1.0
Silica (as Silicate)	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

These ions are added to the bath as the solid chlorides, sulfates, or nitrates wherever possible. All the salts dissolve except that of calcium. The solution is heated, shaken well, and cooled. It is then filtered through a Whatman #40 filter paper to remove the excess calcium salts and the filtrate is used for the accuracy and the precision tests.

Following exactly the recommended routine procedure given near the end of this paper, Table IV shows the results obtained in checking the accuracy of the method. The figures apply to single runs and not to averages of several.

Table IV

Data on Accuracy Test

Micrograms Copper Added	Readings	Average Reading	Blank	Corrected Average Reading	Micrograms Copper Recovered
10	91-89-92	91	48	43	10.8
20	134-136-133	134	48	86	21.5
50	248-248-250	249	48	201	50.5
70	315-320-315	317	48	269	68.0
100	420-425-415	420	35	385	96.0

The average accuracy for all the tests is about 5%. It is somewhat greater for the smaller quantities of copper and smaller for the larger quantities. However, all results show an error of less than 10%.

To furnish an additional check on the accuracy one can attain with the analytical method described below, several commercial laboratories kindly consented to analyze a nickel bath sample containing a known amount of copper using this method. These concerns were the Bethlehem Steel Corporation, Bethlehem, Pa.; Foster D. Snell, Inc., Brooklyn, N.Y.; and the International Nickel Company, New York, N.Y. The bath sample sent out for analysis was the same as that used in the above accuracy test to which enough standard copper solution was added to give it a copper concentration of 10 micrograms per milliliter. The results obtained by these laboratories and the writers on this sample are shown in Table V.

Table V

Results of Check Analyses

Laboratory	Micrograms/ml. of Copper Reported
A	10.0
B	10.0
C	12.0
D	10.2

The results obtained by the four different laboratories agree fairly well indicating that the method when followed closely will give one fairly accurate and reliable results.

To test the precision of the method, four duplicates containing 50 micrograms of copper were run. The results are shown in Table VI.

Table VI

Data Showing Precision of the Method

Micrograms Copper Added	Readings	Average Reading	Blank	Corrected Reading	Micrograms Copper Recovered
50	248-248-250	249	48	201	50.5
50	242-246-244	244	48	196	49.0
50	250-246-246	247	48	199	50.0
50	254-250-248	251	48	203	51.0

The precision of the method is ± 2%. Duplicability of results is as good for other amounts of copper up to 100 micrograms.

Recommended Routine Procedure

The procedure finally adopted for the determination of copper in nickel plating baths is the following:

Solutions Required:

1) Dibutylamine . . . . purest grade obtainable

2) Carbon disulfide . . . . purest grade obtainable

3) 2-Mercaptobenzothiazole solution 1%

Dissolve one gram of the reagent in 100 ml. of ethyl alcohol.

4) Alcohol, ethyl 95%

5) Amyl acetate . . . . reagent grade

6) Standard copper solution . . . . . . 10 micrograms/ml.

Dissolve exactly 100 milligrams of pure copper in a 50 ml. beaker with 1 ml. of concentrated nitric acid. Dilute to a liter and mix. Pipette 10 ml. of this stock solution into a 100 ml. volumetric flask and dilute to the mark with pure distilled water. Each milliliter of this solution contains 10 micrograms of copper.

7) Synthetic Watts type nickel plating bath

330 grams of $NiSO_4 \cdot 7H_2O$, 45 grams of $NiCl_2 \cdot 6H_2O$, and 30 grams of H_3BO_3 are dissolved in pure distilled water to make one liter of solution. These reagents should be of A.C. S. grade.

8) Acetic acid - sodium acetate buffer . . . . . pH = 3.5

Mix 30 ml. of glacial acetic acid with 60 ml. of distilled water and add 12 ml. of 50% sodium acetate (50 g. of the salt in 100 ml. of solution).

9) HCl . . . . (1:1)

10) NH_4OH . . . . (1:1)

Apparatus Required:

1) Separatory funnels - short stemmed Squibb type, of about 60-100 ml. capacity.

2) 25 ml. volumetric flasks

3) Pipettes

4) 25 ml. graduated cylinder

5) Colorimeter or spectrophotometer -- A Klett-Summerson colorimeter with their blue filter No. 42 was used in this investigation. Any other colorimeter with any suitable filter or any spectrophotometer can also be used.

6) Four dropping bottles or eye droppers.

7) 50 ml. beakers

Procedure:

Isolation of the Copper

1) Pipette 5 ml. of the plating bath into a separatory funnel and add 5 ml. of distilled water.

2) Add 2.0 ml. of the acetic acid-sodium acetate buffer.

3) Add 1 ml. of the mercaptobenzothiazole solution and shake well for about 30 seconds.

4) Add 5 ml. of amyl acetate, shake for one minute and then run the aqueous layer into another separatory funnel.

5) Repeat step (4) with another 5 ml. of amyl acetate this time discarding the aqueous layer.

6) Combine the amyl acetate extractions and wash them eight times with 10 ml. portions of pure distilled water.

Development of the Colored System

7) Add 5 drops of dibutyl amine and 2 drops of carbon disulfide.

8) Shake well for 30 seconds and then run the solution into a 25 ml. volumetric flask.

9) Wash the separatory funnel with a few milliliters of 95% ethyl alcohol and run it into the same flask.

10) Dilute the flask to the mark with the ethyl alcohol. Shake well to mix.

Measurement of Light Absorbed by the Solution

11) Using a testtube partially filled with a 1.0 to 1.5 mixture of amyl acetate and ethyl alcohol as the reference liquid, adjust the colorimeter so that the galvanometer pointer is at the zero position when the dial reading is zero.

12) Pour the solution out of the testtube, rinse it out a couple of times with small portions of the test solution and then almost fill the tube with the solution.

13) Put the testtube back in the colorimeter and rotate the dial until the galvanometer pointer returns to its zero position. Record the scale reading.

14) Run a blank following the above procedure exactly except that the additions of the dibutylamine and carbon disulfide are omitted. Record the scale reading.

15) Subtract the blank reading from the test solution reading to get the corrected measure of the light transmitted by the solution. This method of correcting for the blank is permissible only when the scale readings of the instrument used give the extinction of the solution or are related to the extinction, i.e., when the scale is a logarithmic one.

16) Look up the corrected scale reading on the calibration curve, and the amount of copper corresponding to the reading is the quantity of copper in the volume of the bath originally taken for analysis.

If an instrument having a wave length selector is used, set it at 440 millimicrons for this determination.

Calculations

Suppose a reading of 350 is obtained when 5 ml. of a bath are taken for analysis and that a blank on a similar aliquot gives a reading of 46. How much copper is in the bath?

The corrected reading = 350 - 46 = 304. Looking this reading up on the calibration curve shows that it corresponds to the presence of 76 micrograms of copper. Thus there are 76 micrograms of copper in 5 ml. of the bath. Therefore, in a liter of the bath there are 76 x 200 = 15,200 micrograms or 15.2 milligrams of copper. Thus the bath contains 15.2 ppm of copper or 0.0152 grams/liter.

As explained in a previous paper (   ), if a colored system is known to obey Bouguer-Beer's Law, it is possible to eliminate the need for a calibration curve if the instrument used measures transmittancy in terms of extinction or in units related to extinction.

One has only to run a standard containing a known quantity of copper, the unknown, and a blank. After correcting the readings of the standard and the unknown for the blank, the following formula is used to calculate the concentration of copper in the unknown.

$$\frac{\text{Concentration of Standard}}{\text{Corrected scale reading of standard}} \times \text{Corrected reading of unknown} = \text{Concentration of unknown}$$

Discussion

The only critical point in the whole procedure is the adjustment of the pH of the solution. The aqueous layer following the precipitation and the extraction of the copper must have a pH of 2.6 or above. It was found that the pH changed by 0.3 to 0.4 units during the precipitation and extraction steps if the solution is not buffered. The buffer used brings the pH of the solution to about 3.5

A pH of as high as 4.2 will not cause any nickel to be precipitated along with the copper. However, it is best to keep the pH below this figure as other elements--iron--may begin to precipitate out.

Despite the fact that nickel is not apparently precipitated by the 2-mercaptobenzothiazole under the acidity conditions used, it seems to be very difficult to wash the nickel out of the amyl acetate extractions. Even after eight washings with water, a trace of nickel could still be detected in the last washing. However, the quantity remaining was so small that it could not appreciably affect the results obtained.

"Stop and Go" Method for Copper

For those who are interested in a method that will only give approximate results or in a method that can be used without a colorimeter, the following is recommended:

Procedure:

1) Follow the same procedure as that given under the Recommended Routine Procedure up to and including step (9).

2) Then shake the solution and run it into a graduated 50 ml. Nessler tube. Rinse out the funnel with ethyl alcohol and run the washings into the tube. Then dilute the solution with ethyl alcohol to 25 ml.

3) Add to a second Nessler tube 10 ml. of amyl acetate, 5 drops of butylamine, 2 drops of carbon disulfide and enough ethyl alcohol to make the volume in the tube about 24 ml. Shake well to mix.

4) Now add from a microburette, a drop at a time, the copper stock solution described earlier which contains 100 micrograms of copper per milliliter.

5) Shake the solution after each drop is added and compare the color of the solution in this tube to that of the unknown in the other tube. View the two colors horizontally against a white background.

6) Continue steps (4) and (5) until the colors in the two tubes match. Then note the volume of the copper solution added. The amount of copper in the unknown is equal to the amount of copper in the volume of standard solution needed to match the color of the unknown.

Applicability of the Method to Other Types of Nickel Plating Baths

The procedure has been tested on all chloride, 50-50, and high sulfate nickel plating baths as well as on a Watts bath and has been found to give satisfactory results.

Summary

Copper is isolated from the other constituents in the plating bath by precipitation with 2-mercaptobenzothiazole extracting the precipitate with amyl acetate. The color is then developed by adding dibutyl amine and carbon disulfide. After diluting the solution to 25 ml. with ethyl alcohol, the transmittancy of the solution is measured using a Klett-Summerson colorimeter with their #42 blue filter.

FIGURE (1)

Calibration curve for the determination of copper in a Watts type nickel plating bath as copper diethyl dithiocarbamate in a mixture of amyl acetate and ethyl alcohol.

Instrument used -- Klett-Summerson colorimeter with blue filter # 42.

Type cell -- testtube.

Final Volume of Solution -- 25 ml.

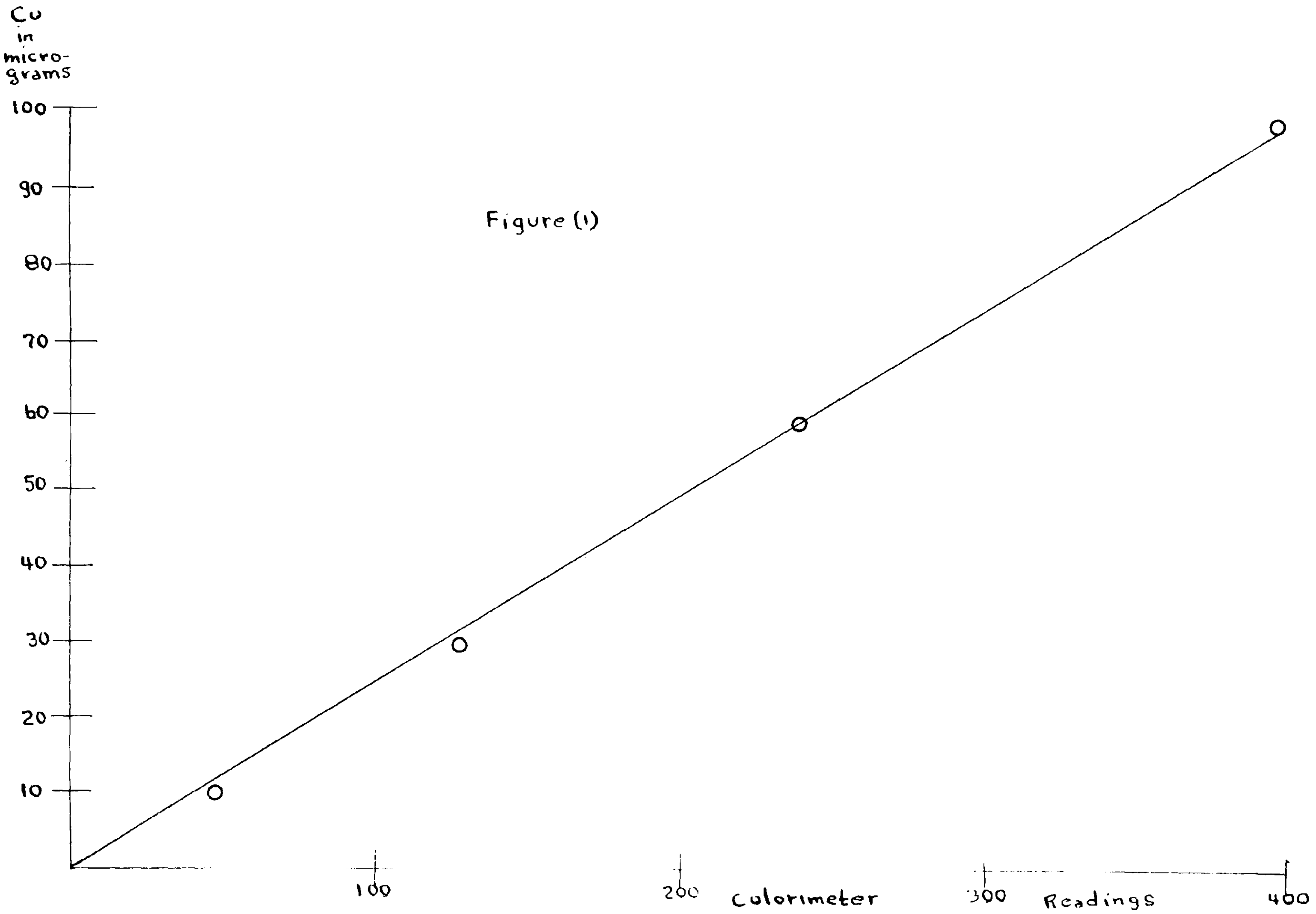


Figure (1)

Cu in micro-grams
100
90
80
70
60
50
40
30
20
10
100
200
300
400
Colorimeter Readings

FIGURE (2)

Curve (a) -- Extinction versus wave length for copper diethyl dithiocarbamate -- 50 micrograms in 25 ml. of solution.

Curve (b) -- Extinction versus wave length for the Klett-Summerson filter #42. The extinction units on the right apply to this curve.

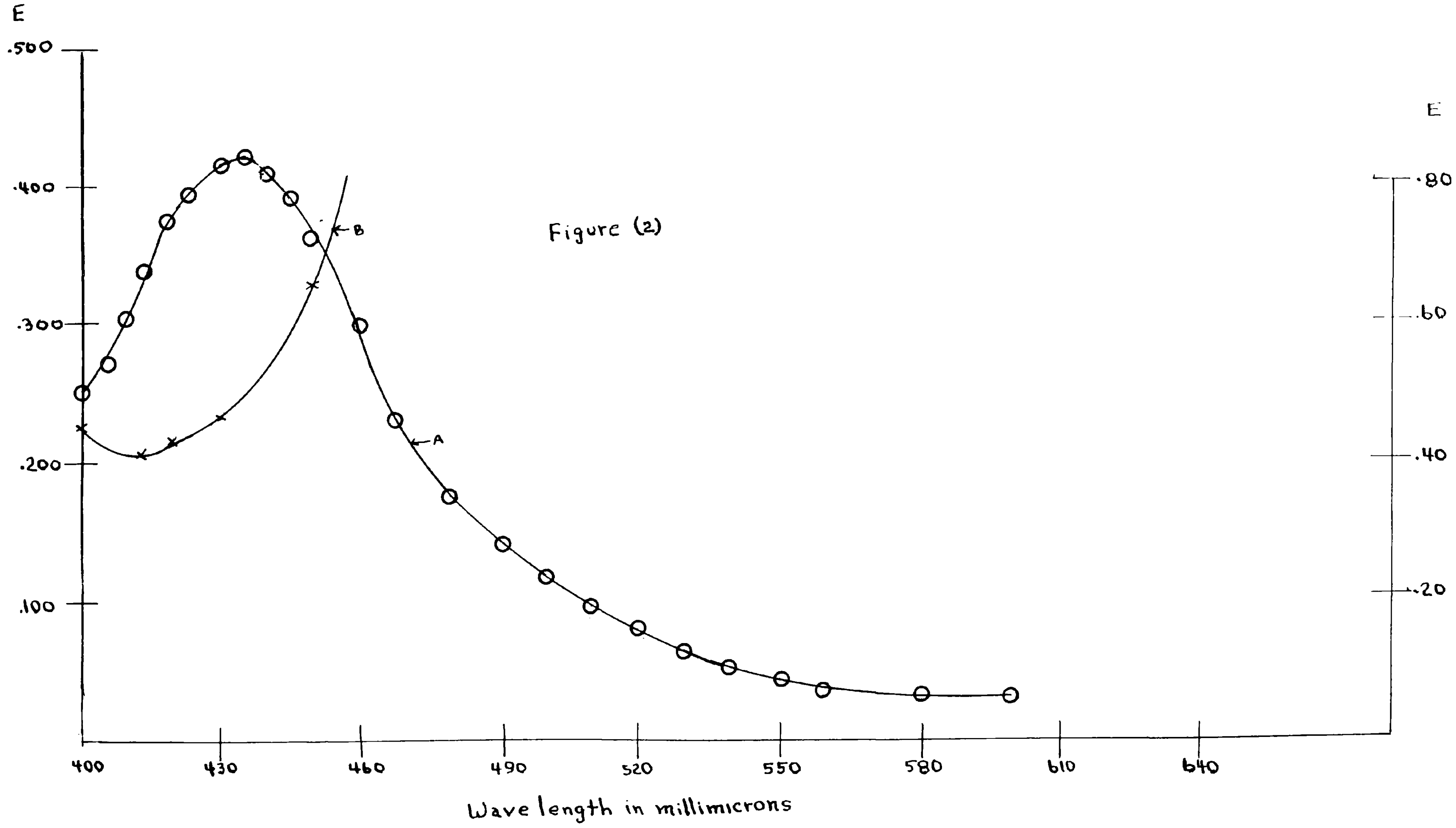


Figure (2)

E
.500
.400
.300
.200
.100
E
.80
.60
.40
.20
B
A
400
430
460
490
520
550
580
610
640
Wave length in millimicrons

SECTION E

THE DETERMINATION OF CADMIUM IN NICKEL PLATING BATHS

THE COLORIMETRIC DETERMINATION OF CADMIUM IN NICKEL PLATING BATHS

The fifth article in this series of investigations on the colorimetric determination of trace elements in nickel plating baths is concerned with cadmium. As before, the method desired is one that will be applicable in the presence of appreciable quantities of lead, iron, chromium, silicon, manganese, copper, zinc, aluminum, and calcium.

A literature survey for methods that have been used for determining cadmium in nickel baths proved fruitless. Also, no references were found for determining cadmium in any type of plating bath except cadmium baths.

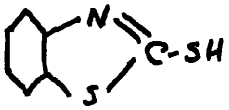
The number of reliable colorimetric methods for determining cadmium are not numerous. The dithizone method described by Fischer and Leopoldi (37, 106) would be satisfactory for this work except for the fact that the cadmium cannot be separated from the nickel by this method even when it is first precipitated as cadmium pyridine thiocyanate.

Small amounts of cadmium can be quantitatively separated for nickel as the sulfide from slightly acid solutions when a collector such as copper is used (30). Cadmium can be determined by precipitation as colloidal cadmium sulfide and then comparing the colloidal suspension, which can be stabilized with gelatin, with a standard. The method is made more sensitive if ultraviolet radiation instead of daylight is used to compare the suspension against the standard (52, 62). However, appreciable quantities of lead would interfere in the analysis of cadmium by this method and therefore it could not be considered further.

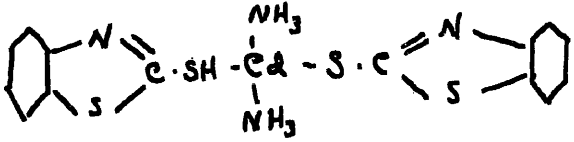
Developmental Work

If cadmium could be separated from nickel, the dithizone method could be used to determine cadmium. Of the other ions in the presence of which the cadmium method is to be applicable, only copper and lead will seriously interfere and their interference can be eliminated. Copper can be removed along with any iron by precipitating it with cupferron and extracting the cupferrides with amyl acetate. Lead interference is prevented by extracting the cadmium from a strongly alkaline solution. Under these conditions lead is not extracted by dithizone.

To find a method of separating cadmium from nickel, a number of reactions of these ions with various organic reagents were reviewed. Of these reagents, mercaptobenzothiazole



seemed to be the most promising. According to Spacu and Kuras (120) who first used the reaction, cadmium in an ammoniacal solution forms a white precipitate with the reagent. The compound formed has the structural formula



according to Prodinger (91). Nickel, however, does not form a precipitate with 2-mercaptobenzothiazole in an ammoniacal solution, and any lead present will be precipitated along with the cadmium but will do no harm as pointed out above.

Spacu and Kuras used the reagent to precipitate several hundred milligrams of cadmium, but it was found that as little as 10 micrograms in a volume of 10 ml. could be precipitated with it. Additional work showed that the separation of cadmium from nickel could be completed by extracting the cadmium mercaptobenzothiazole along with the lead compound with chloroform. It was found to be the best of a number of water immiscible solvents tested for extracting the cadmium precipitate.

To bring the cadmium and any lead present back to an aqueous medium, the chloroform extract is shaken with 6 N HCl. From this point, the determination of cadmium can be completed according to the Fischer and Leopoldi method (37) by extracting the cadmium from a strongly alkaline solution with a carbon tetrachloride solution of dithizone and measuring the extinction or per cent transmission of the solution after dilution to a suitable volume with carbon tetrachloride.

Thus, a tentative procedure was evolved consisting of the following steps:

1) Any copper and iron present are removed by precipitation with cupferron and extraction with amyl acetate.

2) The aqueous solution is made ammoniacal, the cadmium precipitated with mercaptobenzothiazole, and the precipitate is extracted with chloroform.

3) The cadmium is extracted from the chloroform with 6 N HCl, enough NaOH added to make the solution strongly alkaline--about pH = 11--and then the cadmium is extracted with dithizone.

In order to determine whether the tentative procedure was capable of giving quantitative results, 10 micrograms of cadmium were placed in a separatory funnel, 1 ml. of 6 N HCl, 20 ml. of N NaOH added and the cadmium extracted with dithizone solution. The extractions were diluted to 50 ml. with carbon tetrachloride and the transmittancy of the solution measured in the manner described under the Recommended Routine Procedure heading. The reading obtained was considered the "theoretical reading". Then, if a similar quantity of cadmium was carried through the proposed procedure and a similar reading obtained, all the cadmium added was recovered.

When this was done, about 90% of the cadmium added was found; however, when 1 ml. of a pure synthetic Watts type plating bath containing about 90 milligrams of nickel was added to the cadmium, only about 40% of that added was recovered. In addition, a small amount of nickel was still found to be present in the solution after the chloroform extract was shaken with the HCl. A checkup revealed that most of the cadmium loss took place when the chloroform extract was washed with distilled water in order to remove small quantities of nickel in the water droplets suspended in the organic solvent. The cadmium seemed to be extracted from the chloroform layer by the water wash. This did not occur when nickel was absent, but only in its presence.

After a great deal of experimental work, it was found that this loss of cadmium could be eliminated by washing the chloroform extract with an ammoniacal solution of 2-mercaptobenzothiazole. The 2-mercaptobenzothiazole seems to be the effective agent in preventing the return of the cadmium to the aqueous layer. However, even with this washing mixture, a trace of nickel sometimes came through. The addition of dimethylglyoxime before the sodium hydroxide precipitated the trace of nickel and prevented its extraction along with the cadmium by dithizone.

With these changes incorporated into the procedure, cadmium recovery was much better. Table I compares the theoretical reading with that obtained when 10 micrograms of cadmium was mixed with 1 ml. of the synthetic plating bath and the mixture analyzed for cadmium following this procedure.

Table I

Recovery of Cadmium by the New Procedure

Theoretical reading . . .	63
Observed reading	56

Hence, about 90% of the cadmium added is recovered. The 10% lost seems to be due to slight losses in each of the many steps in the procedure.

Preparation of the Calibration Curve

As the results obtained are reproducible and the small amount of cadmium lost is proportional to the quantity present, the procedure is still suitable for a colorimetric method.

The calibration curve is prepared by making a series of successive runs containing 0, 10, 20, 30, 40, and 60 micrograms of cadmium respectively in the presence of 1 ml. of the synthetic nickel bath following the recommended routine procedure given near the end of this paper. The readings obtained are shown in Table II.

Table II

Calibration Curve Data

Micrograms of Cadmium	Readings	Reading	Blank	Corrected Reading	Mean Average Reading
0	19-18-19	18	---	---	---
10	69-67-67	68	18	50	53
10	75-75-72	74	18	56	
10	71-72-68	70	18	52	
20	120-118-115	118	18	100	104
20	122-122-122	122	18	104	
20	128-122-126	125	18	107	
30	172-170-172	171	18	153	153

Table II (Cont'd.)

Micrograms of Cadmium	Readings	Average Reading	Blank	Corrected Reading	Mean Average Reading
40	208-206-206	207	18	189)	
40	208-210-206	208	20	188)	. . 188
40	212-204-206	207	20	187)	
60	286-282-284	284	24	260)	
60	290-298-288	292	24	268)	. . 265
60	288-296-292	292	24	268)	

Beginning with 40 micrograms of cadmium, the blanks became progressively higher because more extractions are required to remove all the cadmium. Three 5 ml. additions of dithizone are sufficient for amounts of cadmium up to 30 micrograms. If necessary, additional extractions are made with 2 ml. portions of dithizone until the last one is colorless or has a light yellowish brown color instead of the bright red color due to cadmium dithizonate.

By plotting the mean average readings against the corresponding amounts of cadmium, the calibration curve shown in Figure 1 is obtained. The fact that it is not a straight line shows that Bouguer-Beer's Law is not obeyed by the colored system over the concentration range tested. This law, however, seems to be followed to about 30 micrograms of cadmium since the curve is practically linear to this point. Fischer and Leopoldi (37) in their original work studied the colored system up to a concentration of 33.3 micrograms of cadmium and found that Bouguer-Beer's Law was followed over this concentration range.

Since there existed the possibility that not all the cadmium was extracted by dithizone or that not all the cadmium was extracted by one portion of HCl from the chloroform solution at the higher concentrations, a few tests were run in which 4^0, 50, and 60 micrograms of cadmium were extracted from a strongly alkaline solution with dithizone. These runs also indicated that Bouguer-Beer's Law was not followed at these concentrations.

The calibration curve data is obtained with a Klett-Summerson colorimeter using the green filter #54 sold with the instrument. If one employs an instrument having a wave length selector, it should be set at about 520 millimicrons since the transmittancy curve for the cadmium dithizonate system (Figure 2a) shows that its absorptiveness is a maximum for light around this wave length. If any other filter colorimeter is used, the filter selected should be one whose maximum transmission band corresponds as closely as possible to that most strongly absorbed by the colored system. Figure 2b shows the transmittancy curve of the filter used in this study and how it compares with that of the cadmium dithizonate solution (Figure 2a). The data for the transmittancy curves in Figure 2 was obtained with a Beckman spectrophotometer.

Accuracy and Precision Attainable

The accuracy with which cadmium can be determined in nickel plating baths with this procedure is illustrated by the following work.

To check the accuracy attainable under conditions similar to those that might be met in plating practice, a commercial bath is simulated by dissolving small amounts of various salts in 100 ml. of a synthetic Watts type plating bath and analyzing for cadmium in the presence of these impurities. Table III shows the ions and the quantity of each that are added.

Table III

Kind and Quantity of Ions Added to the Bath

Ions Added	Quantity in mgs.	Equivalent in grams/liter
Aluminum	100	1.0
Chromate as CrO_3	20	0.2
Copper	20	0.2
Iron as Fe^{+3}	100	1.0
Lead	5	0.05
Manganese	100	1.0
Silicate	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

These ions are added as the solid chlorides, sulfates, or nitrates wherever possible. All the salts dissolved except that of calcium. The solution is heated, shaken well, and cooled. It is then filtered to remove the insoluble calcium salts and the filtrate used for the accuracy and precision tests.

Employing exactly the same procedure as used in preparing the calibration curve, Table IV shows the results one is likely to obtain on single runs.

Table IV

Data on Accuracy Tests

Micrograms Cadmium Added	Readings	Average Reading	Blank	Corrected Average Reading	Micro-grams Cadmium Found	% Error
10	69-67-67	68	17	51	10.0	0
20	110-112-112	111	17	94	18.8	-6.0
30	165-161-161	162	17	145	28.7	-4.3
50	250-248-248	249	20	229	48.7	-3.3
60	288-284-284	285	24	261	57.5	-4.2

The average error in analyzing for cadmium in these tests is 3.7%, while the greatest error is 6%. Hence, if the procedure is closely followed, it should not be too difficult to attain an accuracy of about 6%.

An additional check on the accuracy of the method resulted from sending samples of a test solution to several companies for analysis using the procedure developed. The concerns which kindly consented to do this work were the Bethlehem Steel Corporation, Bethlehem, Pa.; Hanson-Van Winkle-Munning Company, Matawan, N.J.; and the Chrysler Corporation, Detroit, Mich. The test solution was prepared by adding enough cadmium to 100 ml. of the impure synthetic bath used above to give the bath a concentration of 20 micrograms per ml. Their results and those obtained by the writers are shown in Table V.

Table V

Results from Various Laboratories

Laboratory	Micrograms of Cadmium
Bethlehem Steel Corporation	18
Hanson-Van Winkle-Munning Company	19
Chrysler Corporation	20
Lehigh University	18

To illustrate the precision of the method, five duplicate samples containing 20 micrograms of cadmium were run. The results are shown in Table VI.

Table VI

Precision of the Method

Micrograms Cadmium Added	Readings	Average Reading	Blank	Corrected Average Reading	Micro-grams Cadmium Found	% Error
20	112-110-112	111	17	94	18.8	-6.0
20	125-122-122	123	17	106	20.8	+4.0
20	125-120-120	122	17	105	20.7	+3.5
20	112-108-111	110	17	93	18.6	-7.0
20	120-117-118	118	17	101	19.7	-1.5

The precision of the method is fair and the errors of individual runs about the same as that found in the accuracy tests. The average value for the amount of cadmium found is

19.7 micrograms which is a good check.

Recommended Routine Procedure

The following is the procedure finally adopted and recommended for the determination of cadmium in nickel plating baths:

Solutions Required:

1) Cupferron 1%

Dissolve one gram of the reagent in water and dilute to 100 ml. The solution should be kept cold and prepared fresh daily.

2) 2-Mercaptobenzothiazole 1%

Dissolve one gram of the reagent in 100 ml. of absolute alcohol. Prepare the solution fresh each day.

3) Amyl acetate . . . . purest grade

4) Chloroform . . . . purest grade

5) Sodium hydroxide . . . . 1 Normal

Dissolve 40 grams of the C.P. reagent in enough water to make a liter of solution.

6) Hydrochloric acid . . . . about 6 Normal

Mix 98 ml. of concentrated HCl with 102 ml. of H_2O.

7) Dithizone solution . . . . about 0.01%

Dissolve 0.1 gram of purified dithizone in carbon tetrachloride, dilute to one liter and overlay the solution with 10% hydroxylamine hydrochloride. Keep the solution in a cool, dark place to retard oxidation of the reagent. The dithizone can be purified by the method described by the authors in their article on the determination of lead ( ).

8) Carbon tetrachloride . . . . c.p. grade

9) Ammonium hydroxide . . . . c.p. grade

10) Dimethylglyoxime solution 1%

Dissolve one gram of the reagent in absolute alcohol and dilute to 100 ml. This solution should also be prepared daily.

11) 2-Mercaptobenzothiazole + ammonium hydroxide wash solution.

Mix 10 ml. of the 1% mercaptobenzothiazole solution with 10 ml. of concentrated ammonium hydroxide and dilute to 100 ml. with water.

12) Tartaric acid 50%

Dissolve 10 grams of the reagent in H_2O and dilute to 20 ml. Keep in a dropping bottle if one is available.

13) Standard Cadmium Solution . . . . 10 micrograms/ml.

Dissolve 100 mg. of pure cadmium in 1 ml. of conc. HCl. Dilute to a liter. Pipette 10 ml. of this stock solution into a 100 ml. flask, dilute to the mark and shake.

14) Synthetic Watts type plating bath

Dissolve 330 grams of $NiSO_4.7H_2O$, 45 grams of $NiCl_2$, and 30 grams boric acid in pure distilled water and dilute to one liter. Filter to remove any insoluble matter that may be present.

Apparatus Required:

1) Separatory funnels - Squibb type of about 60-100 ml. capacity.

2) Burettes

3) Pipettes

4) Graduates

5) 50 ml. volumetric flask

6) Klett-Summerson colorimeter with green filter #54.

Any suitable photoelectric colorimeter or spectrophotometer may be used if the proper filter or wave length are selected.

7) Funnel and No. 31 Whatman filter paper

8) 50 ml. Erlenmeyer flask.

Procedure:

Separation of Copper and Iron

1) Pipette 1 ml. of the bath into a separatory funnel.

2) Add 5 ml. of cold water and 1 ml. of the chilled cupferron solution. Shake well for about 30 seconds.

3) Add 5 ml. of amyl acetate. Shake well for 30 seconds. After the layers have separated cleanly, run the aqueous layer into another clean separatory funnel.

4) Repeat step (3) running the aqueous solution into a third separatory funnel.

5) Combine the two amyl acetate extracts, add 5 ml. of water, shake for 30 seconds, and after the layers separate, run the wash solution into the funnel containing the sample.

Precipitation of the Cadmium

6) Add two drops of 50% tartaric acid and one ml. of concentrated ammonium hydroxide. The solution should be fairly alkaline.

7) Add one ml. of the mercaptobenzothiazole reagent and shake for about one minute.

8) Add 10 ml. of chloroform and shake vigorously for one minute. Allow the layers to separate and run the chloroform extract into a clean separatory funnel.

9) Repeat step (8) and run the chloroform extract into the same funnel as in step (8). Discard the aqueous layer.

Isolation of the Cadmium

10) Add 10 ml. of the mercaptobenzothiazole-ammonium hydroxide wash solution to the chloroform extracts and shake vigorously for 15 seconds. After the liquid layers separate cleanly, run the chloroform layer into another clean separatory funnel. If there is any solid matter present, take it along with the chloroform solution.

11) Repeat step (10) two more times throwing away the aqueous wash solutions.

12) Add 1 ml. of 6 N HCl and shake the mixture vigorously for about two minutes.

13) Then add 10 ml. of water and shake well for about another minute. Allow the layers to separate and discard the chloroform layer.

Development of the Colored System

14) Add 2 ml. of the dimethylglyoxime solution and shake

for 30 seconds. Allow the mixture to stand for one minute.

15) Run 20 ml. of normal sodium hydroxide into the separatory funnel. Shake for 30 seconds and allow the solution to stand for about a minute to allow any nickel present to precipitate out.

16) Add 5 ml. of the dithizone solution, shake for 30 seconds, allow liquid layers to separate, and then run the extract into a 50 ml. volumetric flask.

17) Repeat the extractions with dithizone until the extract comes through colorless or has a light yellowish brown color. If more than three extractions are required, the subsequent extractions are made with 2 ml. portions of dithizone.

18) Dilute the extracts in the flask with pure carbon tetrachloride, shake well to mix, and then run the solution through a clean Whatman # 31 filter paper. Catch the filtrate in a clean 50 ml. Erlenmeyer flask.

<u>Measuring the Transmittancy of the Solution</u>

19) Using a testtube cell partially filled with carbon tetrachloride as the reference liquid, adjust the colorimeter so that the galvanometer pointer is at its zero position when the dial reading is zero. If the instrument used has a wave length selector, set it at 520 millimicrons.

20) Pour the carbon tetrachloride out of the testtube, rinse it out about twice with small portions of the test solution and then partially fill the tube with it.

21) Simultaneously with the sample run a blank following exactly the same procedure except that no nickel bath aliquot is taken. Use as many extractions with dithizone on the blank as are necessary to extract all the cadmium from the unknown sample.

22) Subtract the blank reading from the sample reading to get a corrected measure of the amount of light transmitted by the solution. This method of correcting for the blank can be used only when the scale readings of the instrument give the extinction of the sample directly or are related to the extinction.

23) Look up the corrected scale reading on the calibration curve and the amount of cadmium corresponding to it is the quantity of cadmium in the volume of bath originally taken for analysis.

Calculations

Suppose 1 ml. of a plating bath is analyzed for cadmium using the procedure just described and a reading of 250 is obtained. Also, assume the blank reading is 20. How much cadmium is present in ppm?

The corrected scale reading is 250 - 20 = 230. According to the calibration curve (Figure 1), this corrected scale reading corresponds to 49.3 micrograms of cadmium. Hence, there are 49.3 micrograms of cadmium in 1 ml. of the plating bath or 49.3 ppm since micrograms per ml. equals parts per million.

Discussion

When copper and iron are removed, the pH of the solution should be around 2.6. If the solution is strongly acid, ammonium hydroxide should be added to bring it to about this value.

One must be careful not to add too little or too much ammonium hydroxide prior to the addition of the mercaptobenzothiazole. In either case, not all the cadmium will be precipitated. The use of 2 ml. of ammonium hydroxide will give low results while about 6 drops of the reagent is just barely enough to give good results.

The tartaric acid is used to prevent the precipitation of ions that form hydrous oxides such as manganese which can result in the formation of a fairly stable emulsion when the cadmium is extracted with chloroform.

The dimethylglyoxime is used to precipitate trace quantities of nickel that comes through from time to time. It should be prepared fresh each day. Erratic results have been obtained when old solutions of the reagent were used.

It is of the utmost importance that all apparatus used in handling the dithizone extracts--funnel, volumetric flask, Erlenmeyer flask, and testtube cells--be well cleaned and tightly stoppered when not in actual use. Cadmium dithizonate is easily decomposed by even dilute acids and enough acid fumes can be absorbed on glassware standing open in the laboratory to cause partial decomposition of the compound.

Failure to watch this factor will lead to erratic results. Any apparatus that has been used for cyanide solutions must not be used as a container for any of the solutions used, particularly those used after the extraction of the cadmium with HCl unless it is cleaned out very thoroughly.

Since the number of extractions required will affect the value of the blank, the blank must be given the same number of extractions as are required to extract all the cadmium from the sample.

Applicability of the Method to Other Types of Plating Baths

The method has been tested on chloride, 50-50, and high sulfate baths as well as Watts type baths and found to give satisfactory results.

"Stop and Go" Procedure

A "Stop and Go" procedure for the estimation of cadmium without the aid of a colorimeter was developed along the lines of the above recommended routine procedure. This technique was somewhat involved and was therefore omitted from this paper. Work is continuing in the laboratory on the development of a simplified "Stop and Go" method for cadmium.

Summary

Copper and iron are removed by precipitation with cupferron and extraction of the cupferrides with amyl acetate.

Cadmium is separated from the nickel by precipitation with mercaptobenzothiazole in an ammoniacal solution and the precipitate is extracted with chloroform. The cadmium is returned to an aqueous medium by shaking the chloroform extract with 6 N hydrochloric acid. The solution is made strongly alkaline with NaOH and the cadmium extracted with a carbon tetrachloride solution of dithizone. After diluting to 50 ml., the extinction of the colored system is measured using light of about 520 millimicrons in wave length or a suitable filter.

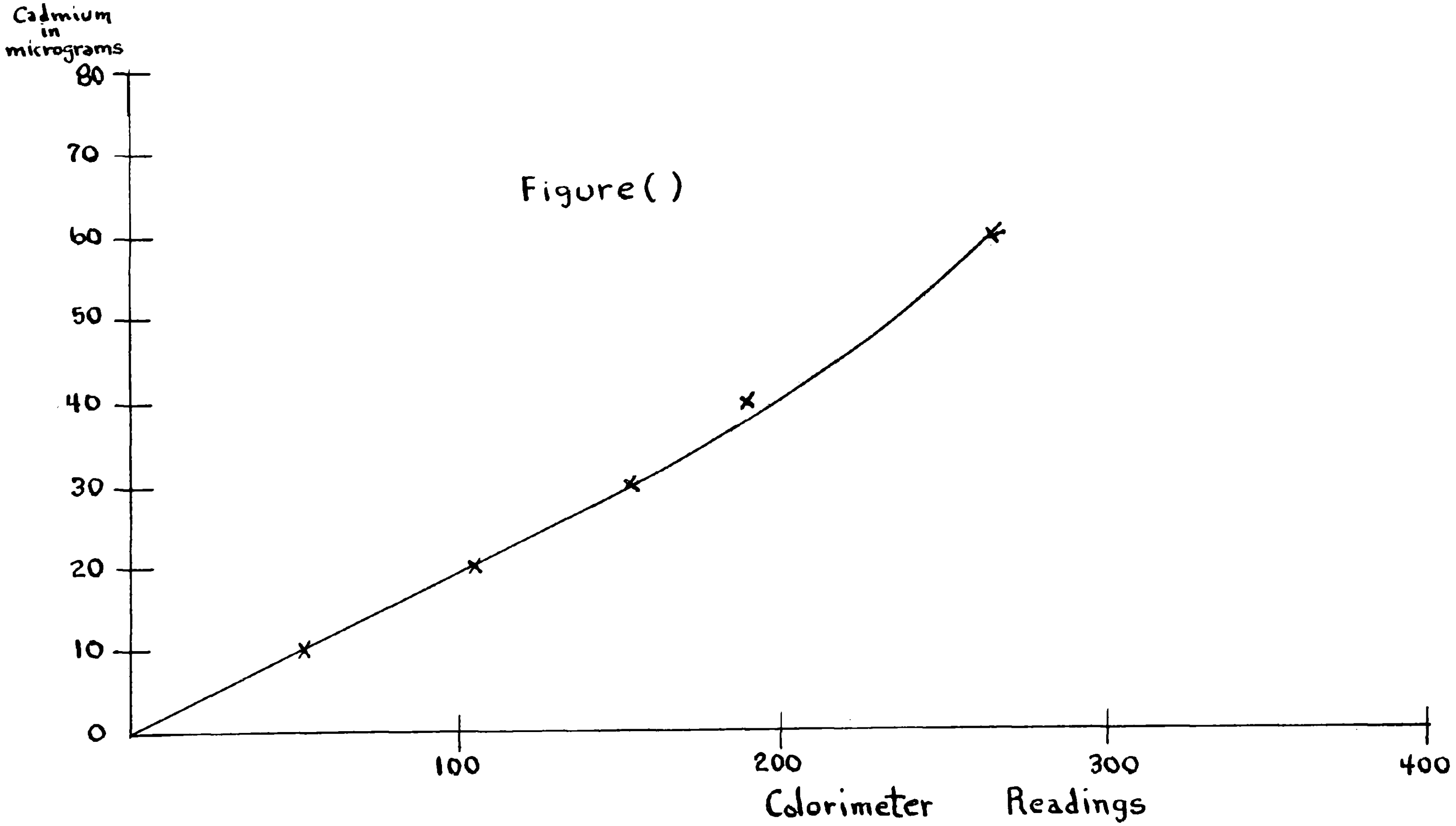
FIGURE (1)

Calibration curve for the determination of cadmium in a Watts type nickel bath by the dithizone method.

Instrument used -- Klett-Summerson colorimeter with green #54 filter.

Cell - testtube.

Final Volume of Solution -- 50 ml.



Figure( )

Cadmium in micrograms
80
70
60
50
40
30
20
10
0
100
200
300
400
Colorimeter Readings

FIGURE (2)

Curve (a) -- Extinction versus wave length for cadmium dithizonate in carbon tetrachloride. 60 micrograms of cadmium in 50 ml. of solution.

Curve (b) -- Extinction versus wave length for the Klett-Summerson green #54 filter. The extinction units on the right apply to this curve.

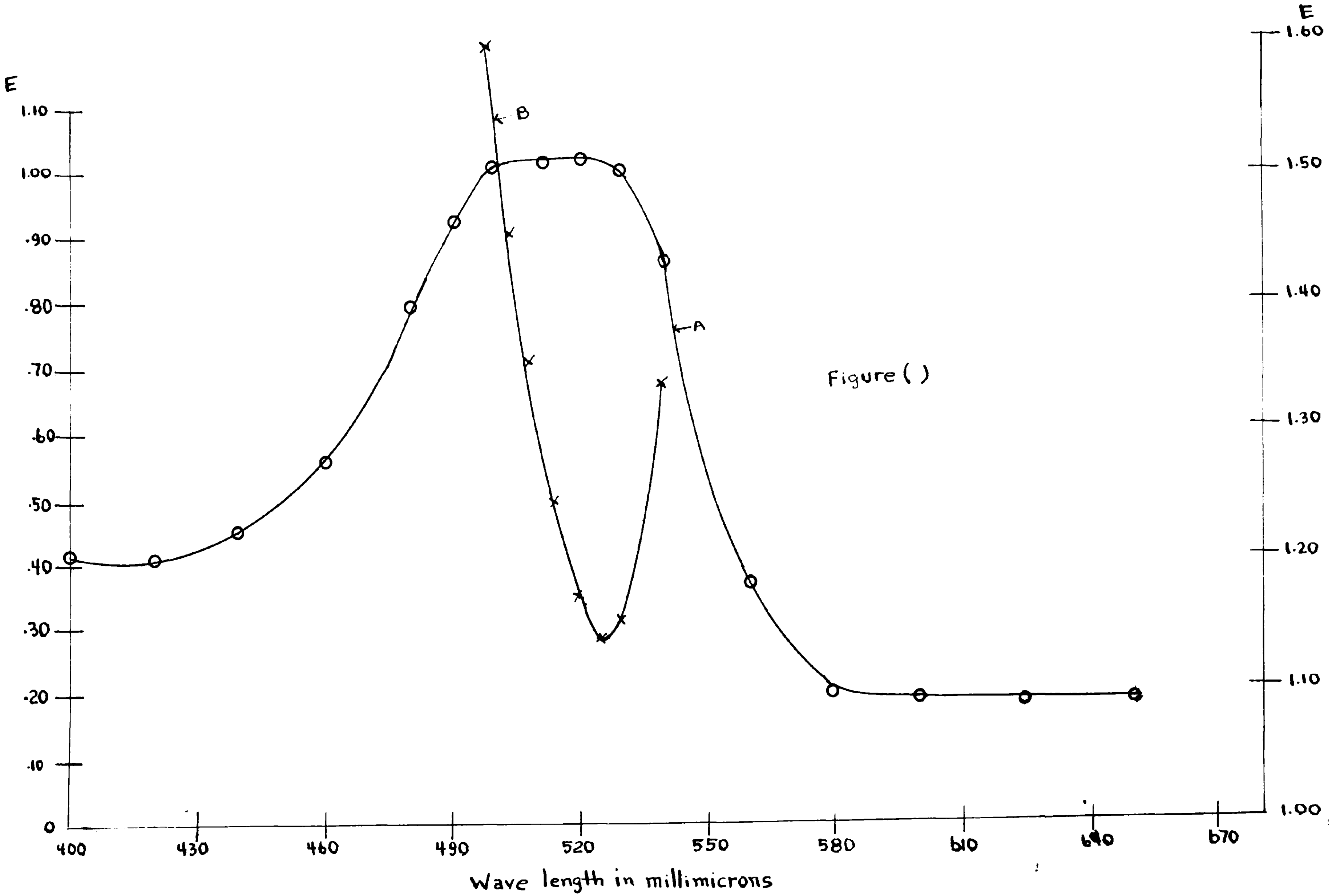


Figure ( )
E
1.10
1.00
.90
.80
.70
.60
.50
.40
.30
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0
E
1.60
1.50
1.40
1.30
1.20
1.10
1.00
B
A
400
430
460
490
520
550
580
610
640
670
Wave length in millimicrons

SECTION F

THE DETERMINATION OF CHROMIUM IN NICKEL PLATING BATHS

THE DETERMINATION OF CHROMIUM IN NICKEL PLATING BATHS

The purpose of this investigation is to develop a rapid, accurate method for the determination of very small amounts of chromium in nickel plating baths when appreciable quantities of aluminum, cadmium, copper, iron, lead, manganese, silicon, zinc, and calcium are present as impurities in the bath.

Although there are many references in the analytical literature pertaining to colorimetric methods for the determination of very small amounts of chromium, there is little information concerning their application to the analysis of chromium in plating baths when it is present as a trace constituent. The use of the diphenylcarbazide method for chromate chromium in nickel and copper plating baths by Foulke (43) was the only one found.

The reaction between hexavalent chromium and diphenylcarbazide to form a strong red-violet colored product was chosen as the basis for a colorimetric method for determining chromium (94, 107, 27, 14).

The method has the following advantages for the purpose in mind:

1) The reaction is very sensitive

2) There are comparatively few other elements that form intensely colored compounds with the reagent. Mo^{+6}, Hg^{+1}, Hg^{+2},

Fe^{+3} and V^{+5} all form colored compounds with the reagent. Iron which may be present in appreciable amounts in plating baths forms a yellow to brown compound with diphenylcarbazide. Its interference can be eliminated by the use of a sufficiently selective green filter as the color absorbs little light above 460 millimicrons while the maximum absorption of the chromate color is about 540 millimicrons.

3) The color is developed in a dilute solution of mineral acid--usually sulfuric--and no buffers, complexing agents, or extractions are required.

Besides the diphenylcarbazide method, the yellow color of the chromate ion itself in alkaline solution is the basis of another common method of determining the ion (63, 94, 107) when the amount present is not too small. It can also be determined as the dichromate ion in an acid solution (27, 119). Other methods involve the reaction of hexavalent chromium with disodium-1,8-dihydroxynaphthalene-3-6-disulfonate (chromotropic salt) to form a red colored solution (45, 69), and the reaction between wool treated with Serichrome Blue R and hexavalent chromium to change the color of the wool from a crimson with a bluish tinge to a dark navy blue whose color intensity will vary with the concentration of the chromate present (119).

This investigation is divided into two parts--to develop a method for the determination of chromate chromium and for determining the total amount of chromium present in the bath.

DETERMINATION OF CHROMATE CHROMIUM

Developmental Work

Since the conditions under which the chromate ion reacts with diphenylcarbazide are so well known, the only problem requiring investigation is the possible interference of the large quantity of nickel and iron that may be present in the bath.

To determine how much interference will be caused by the presence of these ions, six tests were run on the following solutions in individual 25 ml. volumetric flasks.

Run (1) contained 50 micrograms of CrO_3 added as potassium chromate.

Run (2) contained no chromate ion. This was to be a blank on Run (1).

Run (3) contained 0.5 ml. of a pure synthetic Watts type plating bath containing about 90 milligrams of nickel per milliliter in addition to 50 micrograms of CrO_3.

Run (4) contained only 0.5 ml. of the pure synthetic bath.

Run (5) contained 50 micrograms of CrO_3 plus 0.5 ml. of the synthetic bath to which appreciable quantities of all the ions in the presence of which the method is supposed to work was added.

Run (6) was the same as Run (5) except for the addition of the CrO_3.

The diphenyl carbazide reagent was added to each flask and then enough 6 N sulfuric acid so that the acidity of every solution when diluted to 25 ml. was about 0.2 N. Table I shows the readings obtained when the transmittancy of these solutions are measured with a Klett-Summerson colorimeter employing the green filter #54 supplied with the instrument.

Table I

Recovery of Chromate Ion as CrO_3

Run No.	Readings	Blank Corrected Reading
1	417	415
2	2	
3	419	412
4	7	
5	420	406
6	14	

These results show that the presence of the nickel and the impurities added have little effect upon the development of the color of the chromate-diphenylcarbazide complex. Therefore, it should be possible to apply this method without preliminary separations of any constituent.

Preparation of the Calibration Curve

In preparing the calibration curve, 0.5 ml. of the pure synthetic Watts type bath is pipetted into each of six 25 ml.

volumetric flasks, and 0, 5, 10, 25, 30 and 50 micrograms of CrO_3 as chromate ions are added to each flask respectively. Then 1 ml. of the alcoholic 0.25% diphenylcarbazide solution and 1 ml. of 6 N sulfuric acid are added to each flask and the solutions diluted to the mark with pure distilled water.

With distilled water as the reference liquid, the transmittancy of each solution is measured using a Klett-Summerson colorimeter with the green filter #54. This filter was selected because its maximum transmission band is close to the maximum absorption band of the chromate-diphenylcarbazide colored system. The transmittancy curves for the filter and the colored system are shown in Figure 1. The data plotted were obtained with a Beckman spectrophotometer.

Triplicate runs are made at each concentration and the results averaged. The data obtained are shown in Table II.

Table II

Calibration Curve Data

Micrograms CrO_3	Readings	Average Reading	Blank	Corrected Average Reading	Mean Average Reading
0	6-6-6	6			7
0	7-7-6	7			
0	7-8-7	7			
5	48-49-46	48	7	41	41
5	48-48-47	48	7	41	
5	50-47-49	49	7	42	
10	92-90-93	92	7	85	84
10	94-88-92	91	7	84	
10	92-88-91	90	7	83	

Table II (Cont'd.)

Micrograms CrO_3	Readings	Average Readings	Blank	Corrected Average Reading	Mean Average Reading
25	226-220-218	221	7	214)	
25	214-220-214	216	7	209). .	212
25	220-214-222	219	7	212)	
30	256-248-254	253	7	246)	
30	258-252-266	255	7	248) . .	247
30	256-252-254	254	7	247)	
50	425-420-410	418	7	411)	
50	420-415-420	418	7	411) . .	412
50	425-415-420	420	7	413)	

By plotting the mean average readings against the corresponding amounts of CrO_3, the curve shown in Figure 2a is obtained. The resulting straight line shows that Bouguer-Beer's Law is obeyed over the concentration range tested.

Recommended Routine Procedure for Chromate Chromium

The procedure finally adopted for the routine analysis of CrO_3 in nickel plating baths is the following:

Solutions Required:

1) Diphenylcarbazide solution 0.2%

Dissolve 0.2 grams of the reagent in 100 ml. of absolute alcohol. Prepare the reagent fresh every day.

2) Sulfuric acid . . . . about 6 Normal

Dilute 10 ml. of concentrated H_2SO_4 to a volume of 40 ml. Add dilute potassium permanganate to the solution until a faint pink color persists. Cool and dilute to 60 ml.

3) Standard CrO_3 solution . . . . . . 10 micrograms/ml.

Dissolve 147 milligrams of pure potassium dichromate in about 100 ml. of pure distilled water in a liter flask. Dilute to the mark and shake well. Pipette 10 ml. of this stock solution into a 100 ml. volumetric flask and dilute to the mark. Each milliliter contains 10 micrograms of CrO_3.

4) Synthetic Watts type plating bath

330 grams of $NiSO_4 \cdot 7H_2O$, 45 grams of $NiCl_2$ and 30 grams of H_3BO_3 are dissolved in distilled water to make one liter of solution.

5) Nitric acid . . . . c.p. - concentrated

Apparatus Required:

1) Pipettes

2) 25, 100, and 1000 ml. volumetric flasks

3) Colorimeter -- Klett-Summerson colorimeter with the green #54 filter furnished with the instrument. Any other suitable photoelectric colorimeter or spectrophotometer may be used.

Procedure:

1) Using a good fractional pipette, 0.5 ml. of the bath is pipetted into a 25 ml. volumetric flask.

2) Add 2 drops of nitric acid from a dropping bottle and shake the solution well for about a minute. Then add about 15 ml. of distilled water.

3) Add one ml. of the diphenylcarbazide reagent and then 0.8 ml. of the 6 N sulfuric acid. Dilute to the mark and shake well.

4) Using distilled water as the reference liquid, measure the transmittancy of the solution and record the scale reading. Get the reading immediately after diluting and mixing the solution.

5) Simultaneously with the unknown, run a blank in exactly the same manner except for the addition of the diphenylcarbazide reagent.

6) Subtract the scale reading of the blank from that of the sample to get the corrected transmittancy of the solution. This method of correcting for the blank is permissible only when the scale readings of the instrument give the extinction of the solution directly or are related to the extinction--i.e., when the scale is a logarithmic one.

7) Corrected scale reading is looked up on the calibration curve and the amount of CrO_3 corresponding to it is the quantity of CrO_3 in the volume of the bath originally taken for analysis.

DETERMINATION OF TOTAL CHROMIUM

Developmental Work

The simplest method of determining the total concentration of chromium--both hexavalent and trivalent chromium--in nickel baths seemed to be to oxidize the Cr^{+3} to $CrO_4^=$, and then use the diphenylcarbazide reaction to complete the determination. Of the methods available to oxidize Cr^{+++} to $CrO_4^=$ in acid solution, the most commonly used are oxidation with perchloric acid (77, 114, 119) and oxidation with ammonium persulfate in the presence of silver ions (77, 108, 119).

Because of its relative simplicity, the perchloric acid oxidation was tried first, but as feared, the oxidation of very small amounts of chromium was incomplete. In tests with 10 micrograms of reduced $CrO_4^=$, only 50% was oxidized.

Much better results are obtained with the persulfate method. If only chromium is present, all of it is oxidized. However, when 0.5 ml. of the pure synthetic Watts type bath described earlier is added, only about 97% of the chromium present is oxidized.

Calibration Curve for Total Chromium

Because of the incomplete oxidation of trivalent chromium in the presence of nickel, it is necessary to prepare a separate calibration curve for this determination. Although the loss of about 3% of the chromium does not seem like very much, it is enough to make the accuracy attainable with the method poor if the same calibration curve is used for both the chromate and total chromium determination.

To prepare the curve, 0, 10, 20, 30, 40 and 50 micrograms of reduced potassium dichromate are pipetted into individual 50 ml. Erlenmeyer flasks. The solutions are treated as described under the "Recommended Routine Procedure for Total Chromium" heading below. The data obtained are shown in Table III while the curve obtained by plotting the mean average readings against the corresponding quantity of chromium as CrO_3 is shown in Figure 2b.

Table III

Calibration Curve Data for Total Chromium

Micrograms CrO_3	Readings	Average Reading	Blank	Corrected Reading	Mean Average Reading
0	7-8-7	7			7
0	7-7-7	7			
10	88-86-87	87	7	80	80
10	86-85-87	86	7	79	
20	176-174-172	174	7	167	167
20	176-175-172	174	7	167	
30	248-244-248	247	7	240	242
30	252-252-250	251	7	244	
40	340-330-330	333	7	326	326
40	330-330-335	332	7	325	
50	410-405-410	407	7	400	402
50	410-415-405	410	7	403	

Recommended Routine Procedure for Total Chromium

The following has been found to give satisfactory results for the total quantity of chromium in nickel plating baths:

Solution Required:

1) Ammonium persulfate . . . . c.p. grade

2) Amyl acetate . . . . purest grade obtainable

3) Cupferron 1%

Dissolve one gram of the reagent in water and dilute to 100 ml. Keep the solution cool.

4) Sulfuric acid . . . . about 6 Normal

Dilute 10 ml. of concentrated sulfuric acid to 40 ml. Cool and dilute to 60 ml.

5) Perchloric acid 70%

6) Nitric Acid . . . . concentrated

7) Silver nitrate 1%

Dissolve one gram of the c.p. grade salt in water and dilute to 100 ml.

8) HCl . . . . concentrated

9) Diphenylcarbazide solution 0.2%

Dissolve 0.2 grams of the reagent in absolute alcohol and dilute to 100 ml. Prepare the reagent daily.

10) Standard chromium solution . . . 10 micrograms CrO_3/ml.

Dissolve 147 milligrams of pure $K_2Cr_2O_7$ in about 100 ml. of water and dilute to a liter in a volumetric flask. Pipette 10 ml. of this stock solution into a 100 ml. volumetric flask and dilute almost to the mark. Add 1 drop of concentrated H_2SO_4 and a small crystal of sodium sulfite. Shake until the solution appears colorless. Dilute to the mark.

Apparatus Required:

1) Separatory funnels - Squibb type of about 60 ml. capacity.

2) 50 ml. Erlenmeyer flasks

3) Small watch-glasses for covering the flasks

4) Pipettes

5) Dropping bottles

6) Centrifuge

7) Spectrophotometer or colorimeter. Any suitable instrument can be used as explained under the chromate method procedure.

8) Volumetric flasks -- 25, 100, 1000 ml. capacity.

Procedure:

Removal of the Iron

1) Using an accurate fractional pipette, transfer 0.5 ml. of the bath to a separatory funnel.

2) Add 5 ml. of water followed by 1 ml. of cold cupferron. Shake for about 30 seconds.

3) Extract the iron cupferride with 5 ml. of amyl acetate. Transfer the aqueous layer to another separatory funnel and extract a second time with another 5 ml. portion of amyl acetate.

4) Transfer the aqueous layer to a 50 ml. Erlenmeyer flask. Combine the amyl acetate layers and wash with 5 ml. of H_2O.

Run the wash water into the flask containing the sample and discard the amyl acetate extract.

Oxidation of the Chromium

5) Add 2 drops of $HClO_4$, 1 ml. of 6 N H_2SO_4, and 1 ml. of concentrated nitric acid.

6) Mix, place on a hot place, cover the flask with a watch glass and evaporate down just to fumes of perchloric acid or until salts separate out.

7) Cool and wash down cover and sides of flask. Warm the solutions until all the salts redissolve.

8) Add 1 ml. of the silver nitrate solution and then 5 ml. of a ammonium persulfate solution containing 0.3 gram of the reagent.

9) Boil gently for about 10 minutes keeping the volume around 5-7 ml. If it gets below about 5 ml., add a few ml. of distilled water.

10) Add one drop of concentrated hydrochloric acid and digest the mixture until all the permanganate that is formed, if manganese is present, is reduced. This requires from about 3 to 10 minutes. Keep the volume up as described in Step (9).

11) When all the permanganate is reduced, place the flask in a cold water bath to cool.

Development of the Colored System

12) Transfer the solution in the flask to a 25 ml. volumetric flask. Wash the Erlenmeyer flask about 3 times with small portions of distilled water.

13) Add 1 ml. of the diphenylcarbazide solution, dilute to the mark with water and shake well.

14) Almost fill a clean testtube with the solution and centrifuge for two minutes to settle the suspended silver chloride.

15) Pour a portion of the clear supernatant solution into a clean testtube and measure its transmittancy using distilled water as the reference solution. Make the reading without allowing it to stand around.

16) Along with the sample, run a blank in exactly the same manner except for the addition of the diphenylcarbazide.

17) As in the chromate procedure, a Klett-Summerson colorimeter with a green filter #54 is used in measuring the transmittancy of the solution. If the instrument used has a wave length selector, set it at about 540 millimicrons.

Calculations

As in both the chromate and total chromium methods, the element is in the hexavalent state, all calculations are reported in terms of micrograms of CrO_3/ml., ppm of CrO_3, or grams/l. of CrO_3.

Suppose in determining the total chromium concentration of a bath a colorimeter reading of 350 is obtained and a reading of 9 for the blank when a 0.5 ml. aliquot is taken for analysis. How many parts per million of chromium as CrO_3 are present?

Subtracting the blank gives the corrected reading of 350 - 9 = 341. According to the calibration curve for total chromium, this reading corresponds to 42.0 micrograms of CrO_3 in 0.5 ml. of the bath. Then $\frac{42.0 \times 2000}{1000} = 84.0$ milligrams of CrO_3 per liter of bath or 84 ppm of CrO_3.

Since the chromate-diphenylcarbazide colored system follows the Bouguer-Beer's Law, the concentration of CrO_3 in an unknown can be determined without the use of a calibration curve by the application of the equation:

$$\frac{\text{Concentration of Standard}}{\text{Corrected Scale Reading of Standard}} \times \text{Corrected Reading of Unknown} = \text{Concentration of Unknown}$$

This equation can only be applied when the instrument used measures transmittancy in terms of extinction or in units proportional to the extinction.

Accuracy Attainable with the Methods

In order to check the accuracy one can expect when analyzing for chromium by this method under conditions similar to those met in commercial work, small amounts of various salts were dissolved in 100 ml. of the pure synthetic Watts type bath and the accuracy of the procedure determined in the presence of these impurities. Table IV shows the ions and the quantity of each that were added to the bath.

Table IV

Kind and Quantity of Ions Added to the Bath

Metal Ion Added	Quantity added in mg.	Equivalent in grams/l.
Aluminum	100	1.0
Cadmium	100	1.0
Copper	20	0.2
Lead	5	0.05
Manganese	100	1.0
Silicon as $SiO_3^=$	100	1.0
Zinc	100	1.0
Calcium	saturated	saturated

These ions are added as the solid chlorides, sulfates, or nitrates wherever possible. All the salts dissolve completely except that of calcium. The mixture is heated, shaken well, and then cooled. It is then filtered to remove insoluble salts and the filtrate used for the precision as well as accuracy tests.

Employing the procedures described under "Recommended Routine Procedure" headings, Table V shows the results obtained on single runs with both the chromate and total chromium procedures.

Table V

Data Showing Accuracy Obtained

Micrograms of CrO_3 added	5	10	20	25	30	35	40	50
Micrograms found using total chromium method		9.0	18.9		27.6		36.8	46.5
Micrograms found using chromate method	5.0	9.1		24.8		34.2		49.3

The average accuracy of the chromate method is about 3% while that of the total chromium method is about 7.7%. The greater error in the total chromium procedure is not due to the relative length of the procedure and the many steps involved as a pure chromium solution treated according to the procedure will give 100% recovery. It seems that the presence of the impurities after strong oxidation somehow cuts down the intensity of the color formed. However, both procedures will give results that will be accurate to better than 10%.

An additional check on the accuracy that can be expected from the procedures resulted from sending samples of a test solution to several concerns for analysis using these methods. The organizations which kindly consented to test the methods were the Bethlehem Steel Corporation, Bethlehem, Pa.; Foster D. Snell, Inc., Brooklyn, N.Y.; and the Bell Telephone Laboratories, New York, N.Y. The test solution was prepared by adding enough chromate and reduced chromate to 100 ml. of the impure bath used above to give it a total CrO_3 concentration of about 50 micrograms/ml. of bath. Their results and those obtained by the writers are shown in Table VI.

Table VI

Results Obtained by Cooperating Laboratories

Laboratory	Micrograms/ml of chromate chromium	Micrograms/ml of total chromium
Bethlehem Steel Corp.		
Foster D. Snell, Inc.		
Beel Telephone Labs.		
Lehigh University		

The results obtained show that all the laboratories checked each other as satisfactorily as can be expected when four different laboratories--three of them unfamiliar with the procedure--try to check each other.

Precision of the Methods

To test the precision of the methods, a series of duplicates were run using the same bath as prepared for the accuracy tests. The results obtained are shown in Table VII.

Table VII

Precision Data

Chromate Method		Total Chromium Method	
CrO_3 Added	CrO_3 Found	CrO_3 Added	CrO_3 Found
25 micrograms	24.8 micrograms	50 micrograms	47.0 micrograms
25	24.3	50	46.5
25	24.4	50	47.6
25	24.6	50	46.5
25	24.4		

Although the results tend to run slightly low, duplication is pretty good. Runs made weeks apart duplicate each other nicely when the procedure is closely followed.

Discussion

If one does not have an accurate fractional pipette on hand for taking a 0.5 ml. aliquot, transfer 10 ml. of the bath to a 100 ml. flask and use 5 ml. of the solution for the determination. If more than 50 micrograms of CrO_3 are present in 0.5 ml. of the bath, a smaller aliquot should be taken and the determination repeated.

In the total chromium method, the most critical points are:

1) Be certain to keep the volume of the solution during oxidation and during the reduction of any manganese around 5 ml. at the least. If it goes down below this volume, low, erratic results will be obtained. On the other hand, the volume must not be too high as the persulfate oxidation will be slower and the time required for complete reduction of any manganese present greatly lengthened due to the formation of increased quantities of MnO_2. However, the latter point does not appreciably affect the results obtained as much as too low a volume does.

2) The freshness of the diphenylcarbazide solution. Low results were obtained with solutions of the reagent that were several days old. On standing, the solution changes in

color from a pale pink to a deep red. If it has a strong red color, it is best to discard it and prepare a fresh solution.

The purpose of the cupferron + amyl acetate treatment is to remove all the iron present. Ferric iron will react with diphenylcarbazide to form a yellow brown compound which absorbs some of the light transmitted by the green filter used. It is an odd fact that the same quantity of ferric ion added as $FeCl_3$ increases the blank reading in the chromate method by 7 scale division, but in the total chromium method by as many as 20 scale divisions. Therefore, if the iron is not removed in the total chromium method, the accuracy of the determination is at the mercy of the iron content if it is unknown. In the chromate chromium method, the comparatively large amount of iron only results in a possible error of 7 scale divisions which is equivalent to less than one microgram of CrO_3. Hence, it is not removed in this method.

The acidity of the final solution should be as close to 0.2 normal as possible. If the acidity is much lower, the maximum color will develop only slowly, while if too high, the color becomes more unstable. It is better to use sulfuric instead of hydrochloric since the color of any iron present will be intensified with the latter. If the acidity is at 0.2 normal, the color will develop to a maximum intensity within a few seconds. It is not perfectly stable for long periods of time, but slowly decreases in intensity. In a half hour after mixing, the decrease is already appreciable.

Hence, try to get the reading about the same time after mixing.

"Stop and Go" Method for Chromium

For those who want a visual comparison method for determining chromium, the following is recommended:

1) Develop the color in an unknown and a blank in the same manner as described in the Recommended Routine Procedures.

2) Transfer the solutions in the 25 ml. flasks to 50 ml. Nessler tubes. The blank should only be diluted to about 23 ml.

3) Then add standard chromate solution from a burette to the blank with thorough mixing following each addition until the colors of the solutions in the tubes match when viewed transversely against a white background. The unknown then contains as much CrO_3 as is added to the blank solution.

For total chromium, allow the solutions to set for a few minutes after each addition of the standard solution so that most of the silver chloride precipitate has a chance to settle before comparing the colors of the solutions.

Applicability of the Methods to Other Types of Nickel Baths

The methods have been tested on 50-50, chloride, and high sulfate type baths as well as on Watts type baths and have given satisfactory results.

Summary

Methods for the determination of chromate chromium and total chromium in nickel plating baths have been developed. For chromate chromium, the aliquot is transferred to a volumetric flask, a little nitric acid added to oxidize any reducing agents, diphenylcarbazide added and the acidity adjusted with 6 N H_2SO_4 so that the final solution diluted to the mark is 0.2 normal. The transmittancy of the solution is measured and the amount of CrO_3 present as chromate read off the calibration curve. For total chromium, any iron present is removed by precipitation with cupferron and extraction with amyl acetate. Organic compounds, reducing agents and chlorides are next removed by evaporating the solution down until salts separate out. The chromium is oxidized with ammonium persulfate in the presence of silver ions and the silver precipitated with excess HCl which also reduces any oxidized manganese. The solution is centrifuged, the transmittancy of the clear supernatant solution measured, and the amount of CrO_3 present as both Cr^{+++} and $CrO_4^{=}$ read off the calibration curve.

FIGURE (1)

Calibration curves for the determination of chromate and total chromium in a Watts type nickel bath by the diphenylcarbazide method.

1) Curve (a) - Calibration curve for chromate chromium.

2) Curve (b) - Calibration curve for total chromium.

Instrument used - Klett-Summerson colorimeter with green #54 filter.

Cell - testtube.

Final Volume of Solution -- 25 ml.

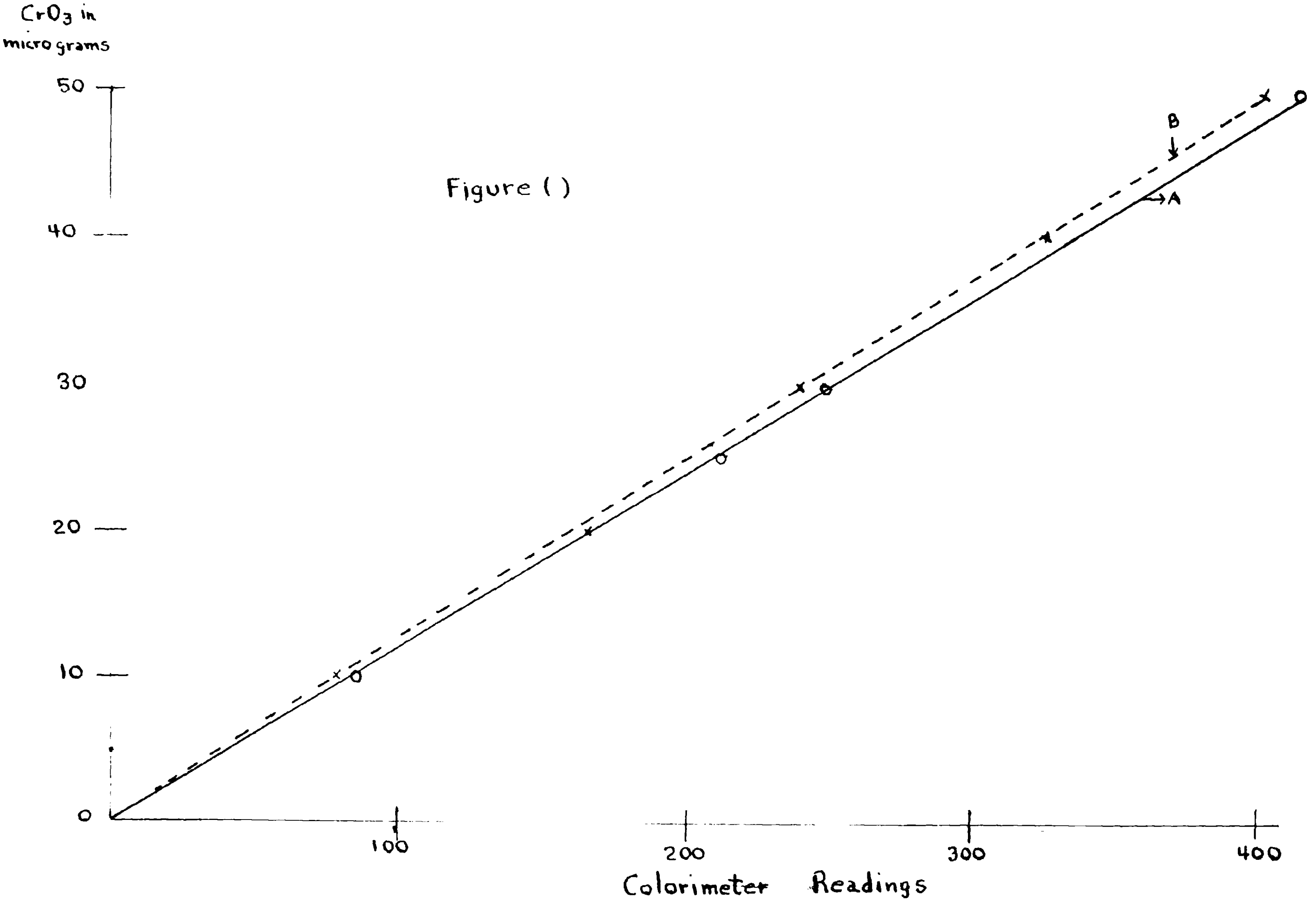


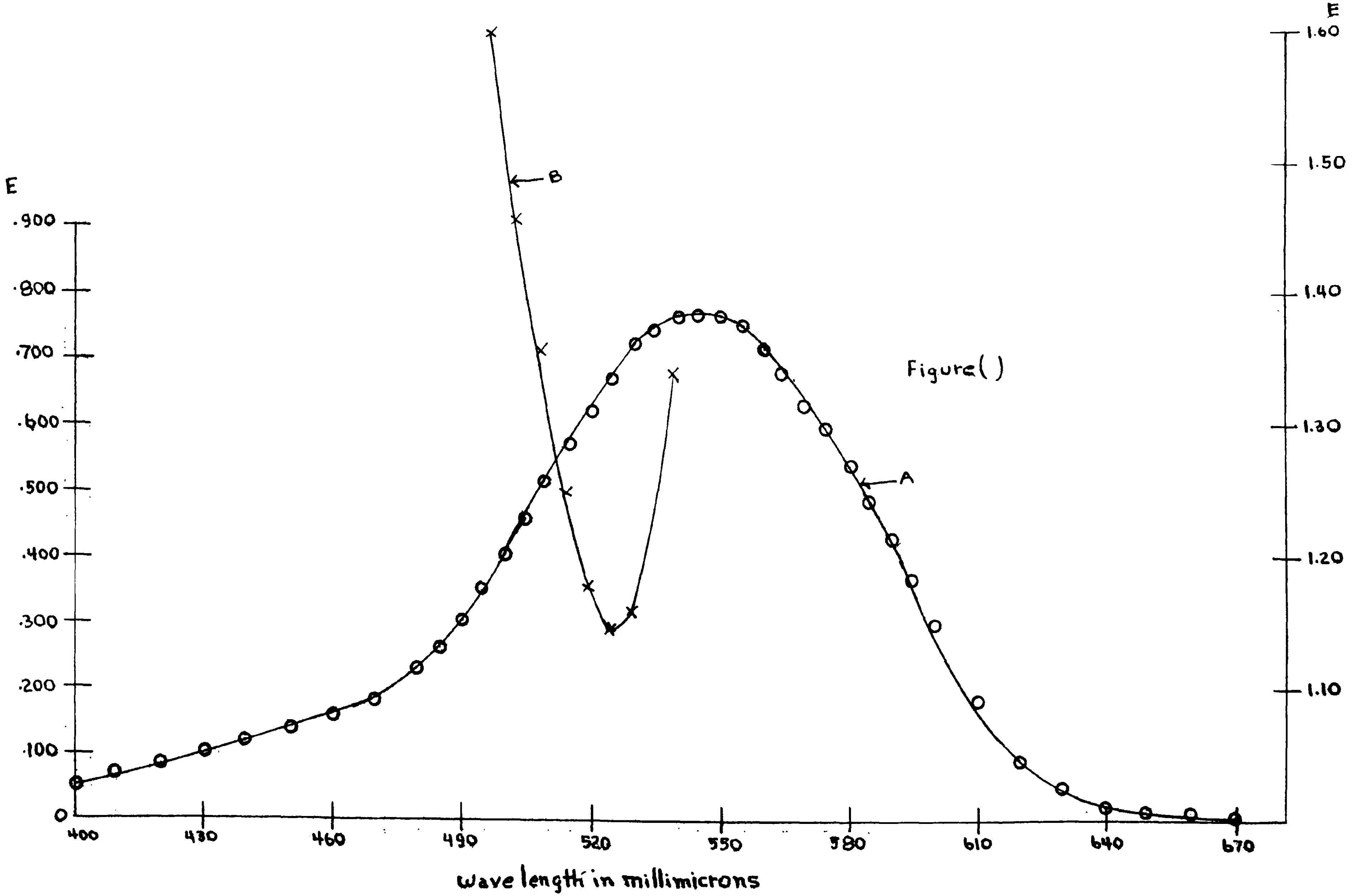
Figure ( )

CrO_3 in micro grams
50
40
30
20
10
0
100
200
300
400
Colorimeter Readings
B
A

FIGURE (2)

Curve (a) -- Extinction versus wave length for the chromate-diphenylcarbazide complex. Concentration is 50 micrograms of CrO_3 per 25 ml. of solutions.

Curve (b) -- Extinction versus wave length for the Klett-Summerson green #54 filter. The extinction units on the right apply to this curve.



Figure( )

E
.900
.800
.700
.600
.500
.400
.300
.200
.100
0
E
1.60
1.50
1.40
1.30
1.20
1.10
400
430
460
490
520
550
580
610
640
670
wave length in millimicrons
A
B

SECTION G

THE DETERMINATION OF ZINC IN NICKEL PLATING BATHS

DETERMINATION OF ZINC TRACES IN NICKEL PLATING BATHS

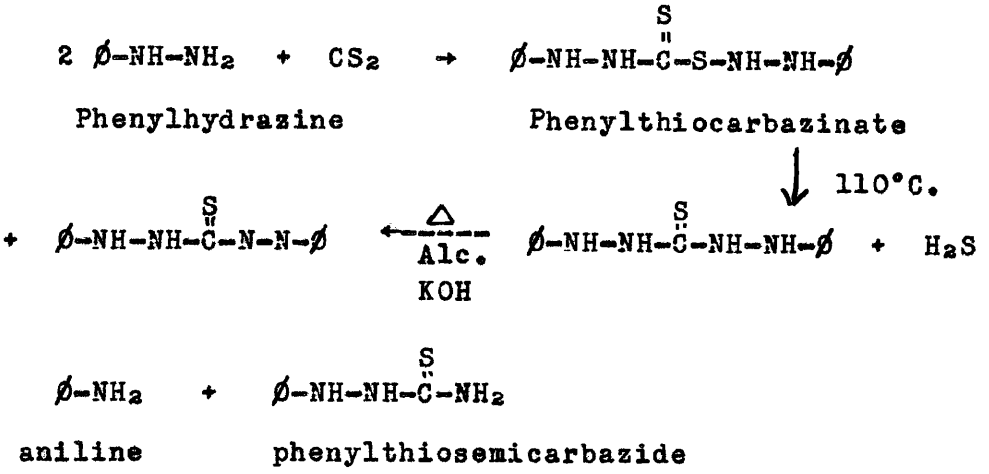
The purpose of this investigation was to develop a method for the determination of traces of zinc in nickel plating baths. Other metallic ions present in commercial baths as impurities were assumed to be present in appreciable amounts. Thus, any method finally developed had to be applicable in the presence of these impurities.

A literature search was made for methods of analysis of nickel plating baths for zinc, and although none were found, it is assumed that many commercial laboratories use their own unpublished methods. However, the literature abounds in methods for determining traces of zinc in many other materials, such as water, biological matter, foods, beverages, rocks, soil, steel, etc. (1, 9, 10, 16, 24, 54, 55, 71, 82, 95, 109, 78).

A study of the various methods was made with the result that a colorimetric method seemed most practical for the purposes of this investigation. Turbidimetric methods were considered (11, 89, 133), but were thought to be less accurate. Polarographic as well as spectrographic methods were eliminated immediately because of the expensive equipment required and volumetric methods (29, 70) were not sensitive enough. Of the turbidimetric methods, those of Hibbord (54), Birkner (9), Bodansky (10), Mildrum (82), Boggs and Alben (11), etc., used potassium ferrocyanide, forming zinc ferrocyanide, a white precipitate which was measured in a nephelometer or photometer. Isbell (61) obtained a $ZnHg(SCN)_4$ precipitate formed by mercuric ammonium thiocyanate, and estimated zinc by comparison with a set of standards. These methods are not satisfactory in the presence of the interfering ions present in a nickel plating bath. Indirect colorimetric methods such as that of Teitlebaum (122) and Lott (74) who precipitated zinc with 5-nitroquinaldic acid, after removal of impurities, followed by reduction to an orange colored water soluble compound, appeared to be too involved. Also the removal of all impurities seemed too difficult for our problem.

The most widely used colorimetric methods for the determination of zinc traces involve the use of diphenylthiocarbazone, commonly referred to as "dithizone". This reagent gives the most sensitive color test with zinc thus far known. Since most other metals also form compounds with dithizone, it is necessary to either remove, or render inactive, the ions of metals present as impurities. Since the literature provided several methods involving its use in the presence of various interfering metallic ions (24, 36, 57, 95, 108, 112, 55), a study of these methods was made.

Dithizone was first studied as an analytical reagent by H. Fischer in 1925 (32), although it had been prepared as early as 1878 by Emil Fischer (31). The following reactions show its preparation, beginning with phenylhydrazine and carbon disulfide:



$$2\ \phi\text{-NH-NH}_2 \ + \ CS_2 \ \rightarrow \ \phi\text{-NH-NH-}\overset{S}{\overset{\|}{C}}\text{-S-NH-NH-}\phi$$

Phenylhydrazine Phenylthiocarbazinate

$$\downarrow \ 110°C.$$

$$+ \ \phi\text{-NH-NH-}\overset{S}{\overset{\|}{C}}\text{-N-N-}\phi \ \xleftarrow[\text{Alc. KOH}]{\Delta} \ \phi\text{-NH-NH-}\overset{S}{\overset{\|}{C}}\text{-NH-NH-}\phi \ + \ H_2S$$

$$\phi\text{-NH}_2 \ + \ \phi\text{-NH-NH-}\overset{S}{\overset{\|}{C}}\text{-NH}_2$$

aniline phenylthiosemicarbazide

The dithizone is separated from the aniline and phenylthiosemicarbazide by-products by dissolving it in dilute alkali and reprecipitating with weak acid. The commercially prepared reagent is generally repurified just before making up a chloroform or carbon tetrachloride solution for analytical work (127). Metallic ions which give distinctive reactions with dithizone are: copper, silver, gold, cadmium, mercury, thallium (ous), tin (ous), lead, bismuth, manganese (ous), cobalt, nickel, palladium, and platinum, in addition to zinc (35). However, all do not form stable dithizonates at the same pH. The structure of the zinc dithizonate molecule is not definitely known, but the dithizone molecule usually acts as a monobasic acid, forming metal dithizonates by replacement of one of the hydrogens in the group (S-C-NH-NH-). Some type of ring formation may occur, increasing the valence of the dithizone radical to two, but lead dithizonate is known to have the formula, PbD_2, where D is the monovalent dithizone radical (127). The pH at which dithizone reacts quantitatively with zinc is in the range 8.5 to 9.0, although it is also possible to obtain good results on the acid side at pH 4.75. The method of Sandell (95) and others (36, 109) employs sodium thiosulfate as a complexing agent which prevents the reaction of metallic ions other than zinc, with dithizone at pH 4.0 to 5.5. These methods, however, require different amounts of $Na_2S_2O_3$ for different amounts of impurities, since an excess would also tend to complex the zinc. The results obtained showed that copper, cadmium, and nickel interfered. Fischer and Leopoldi (36) used 5% KCN in addition to thiosulfate to eliminate the interference of nickel and cobalt. At a pH of 8.5 to 9.0, Holland and Ritchie (57) reported that sodium diethyldithiocarbamate would inhibit the reaction of all metals with dithizone except zinc. Their data showed good results in the presence of 100 micrograms of each of the following elements: calcium, lead, mercury, bismuth, cobalt, tin, and nickel. Only cadmium caused high results and should be removed before the addition of dithizone. This method was a mixed color method. Others, such as Cowling and Miller (24), used this reagent in determining zinc in biological materials, silicate rocks (95), soils (109), etc. (3). Hibbard (55) described a mono color method, in which the excess dithizone solution, which is green, is removed from the red zinc dithizonate solution by the use of .02 N ammonium hydroxide. Another approach was made by Sherman and McHargue (112) who recommended the removal of all interfering metals by their reaction with organic reagents and extracting the compounds thus formed with suitable organic solvents. Owing to the large amount of nickel in the plating bath samples, this method would involve too large a number of extractions for practical work. This method would probably yield the best results if not for the objection mentioned. Thus, it was decided to attempt to develop a method in which the nickel and other metallic ions present could be complexed, or removed by a small number of extractions, and the zinc reacted with dithizone.

Developmental Work

A successful method was finally developed involving a modification of the mono color method of Cowling and Miller (24). In place of the diethyldithiocarbamate, diethanoldithiocarbamate was chosen as a complexing agent in the hope that better results would be obtained. First, tests were made using distilled water to which varying quantities of zinc were added and as these appeared to give satisfactory results, a nickel bath of the 50-50 type was made up for testing. Tests were made to determine whether the complexing agent could inhibit the large amount of nickel ion present, and yield good results for zinc. The reagent formed a precipitate with the nickel when a 0.1 ml. sample of the bath was diluted to about 50 ml. with distilled water, and treated with an excess of reagent. It was found that the reagent if adjusted carefully to pH 8.8 when made up could be used as a buffer in addition to a complexing agent, in stripping the excess dithizone from the carbon tetrachloride layer. For these and all subsequent tests, a standard zinc solution was made up and stored in a pyrex flask. One hundred milligrams of pure zinc metal were dissolved in 10 ml. of (1:1) HCl and diluted to a liter with zinc-free distilled water. One ml. of this stock solution was diluted to 100 ml. to obtain a working solution containing 1 microgram of zinc per milliliter. The tests made using the pure bath were found to give satisfactory results.

Next, a 50-50 nickel plating bath was made up to contain the interfering metallic ions which may be expected to be present in a commercial nickel plating bath. These are shown in Table I. For the tests with this nickel bath plus "impurities" it was decided to use cupferron to remove the iron and copper ions. A 1% aqueous solution of cupferron was added to a 0.1 ml. sample of the nickel bath diluted with 25 ml. of distilled, zinc-free water. The cupferrides formed quickly on shaking, and were extracted with two 10 ml. portions of amyl acetate. The clear aqueous solution then contained the remaining metallic ions. These were complexed with the reagent, and a carbon tetrachloride solution of dithizone was used to form the red zinc dithizonate. The excess dithizone was extracted by shaking with water and another portion of reagent. If the excess was too large to be removed by one extraction to give the pure red color, a wash solution of dilute NH_4OH was used to extract the remainder.

Table I

Impurities Added to 50-50 Nickel Bath

Constituent	Mg. added per liter	Added As
Al^{+++}	100	$Al_2(SO_4)_3.18H_2O$
Cd^{++}	100	$CdCl_2.2\ 1/2\ H_2O$
Cr^{+++}	20	CrO_3
Cu^{++}	20	$CuCl_2.2H_2O$
SiO_2	100	Na_2SiO_3
Fe^{+++}	100	$FeCl_3.6H_2O$
Pb^{++}	5	$Pb(C_2H_3O_2)_2.2H_2O$
Mn^{++}	100	$MnCl_2.4H_2O$
Ca^{++}	saturated	$CaCl_2$

- The 50-50 bath contained 181 g. $NiSO_4.6H_2O$, 97.2 g. $NiCl_2.6H_2O$ and 30 g. boric acid per liter of solution.

The name reagent was first made up using diethanolamine and carbon disulfide, diluting with water and adjusting to pH 8.8 using a Beckman pH meter. The sodium salt may now be obtained commercially #. This salt was found to be completely satisfactory for the procedure as finally developed. During the tests, it was found that the pH must be maintained as close to 8.8 as possible, or at any rate between 8.5 and 9.0. If the solution becomes too alkaline, low results will be obtained. Another difficulty experienced before satisfactorily

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- J. T. Baker Chemical Company, Phillipsburg, N.J.

consistent results could be obtained was the contamination of reagents and equipment with residual zinc. Low blanks were obtained only after purifying nearly all reagents, and exercising the utmost care in cleaning glassware. All separatory funnels and other glassware must be frequently cleaned with nitric acid or cleaning solution, and thoroughly rinsed with zinc-free distilled water five or six times. In the final procedure adopted, 2 ml. of 10% tartrate was added to the aqueous solution before addition of the complexing agent. This was done in order to prevent precipitation of the hydrous oxides present and aid in maintaining the proper pH.

After numerous tests with varying amounts of zinc, from 1 to 20 micrograms, satisfactory results were obtained and a calibration curve was made up for use in obtaining final data for the accuracy and precision of the routine method. The exact procedure followed is described under "Recommended Routine Procedure".

Preparation of the Calibration Curve

Known amounts of standard zinc solution were added to 0.1 ml. samples of pure 50-50 nickel plating bath. These samples were run through the regular procedure and the values obtained on the colorimeter were corrected for the blank. These corrected colorimeter readings were then plotted against the corresponding amount of zinc which had been added. A straight line which passed through the origin was obtained, showing that Bouguer-Beer's Law is obeyed over the range tested (Figure 1).

Since there were no impurities present in these runs, the use of cupferron and the amyl acetate extractions were omitted. The values plotted for each point was the average of three separate determinations, thus giving a more nearly correct value. The curve could then be used in reading off the zinc present in unknown samples. Table II gives the calibration curve data. A Klett-Summerson colorimeter with a #54 green filter was used for all colorimetric measurements. However, any colorimeter with the proper filter may be used. If a spectrophotometer is available, its wave length dial should be set at a wave length of 535 millimicrons. The maximum absorption wave length of the red zinc dithizonate was obtained by plotting wave length versus extinction for a 5 microgram sample of zinc converted to zinc dithizonate in 25 ml. of CCl_4 solvent. This was done over the range 400 to 600 millimicrons, and a maximum was found at 535 millimicrons. The curve was compared with a similar curve obtained for the green #54 filter. It was found that this filter transmits the maximum amount of light at wave length 520 to 540 millimicrons. Hence, this filter gives the greatest sensitivity to changes in concentration, since it passes only light of the wave length most highly absorbed by the sample. The curves are shown in Figure 2. A Beckman ultraviolet spectrophotometer, using 1 cm. corex cells with CCl_4 as a reference liquid, was used in obtaining the curves.

Table II

Calibration Curve Data

Micrograms Zinc Added	Colorimeter Reading Obtained	Blank Reading	Corrected Colorimeter Reading	Average Reading
Blank	33	——	———	———
Blank	34	——	———	———
Blank	32	——	———	———
2	59	33	26	———
2	58	33	25	25
2	58	33	25	———
5	92	33	59	———
5	93	33	60	61
5	96	33	63	———
10	153	33	120	———
10	158	33	125	123
10	158	33	125	———
15	220	33	187	———
15	218	33	185	187
15	222	33	189	———
20	320	72	248	———
20	318	72	246	250
20	330	72	258	———

Recommended Routine Procedure

The procedure finally adopted for the colorimetric determination of zinc in nickel plating baths is as follows:

Solutions Required:

1) Cupferron 1%

Dissolve 1 gram in 100 ml. of zinc-free distilled water. This solution discolors on exposure to light and should be made up fresh daily.

2) Amyl acetate . . . . purest grade

Residual zinc may be removed by washing the reagent with dilute HCl several times followed by 8 to 10 washings with zinc-free distilled water.

3) Sodium tartrate 10%

Dissolve 10 grams of sodium tartrate in 100 ml. of zinc-free distilled water. Purify by shaking with three portions of dithizone.

4) Name reagent # .

Dissolve 30 g. of sodium (2-hydroxyethyl) dithiocarbamate (sodium salt of diethanoldithiocarbamate) in 60 ml. of zinc free distilled water in a 150 ml. beaker. Add 1 ml. of concentrated ammonium hydroxide. Now adjust the pH of this solution to about 8.8 - 8.9 with a 25% solution of ammonium chloride. Around 10 ml. of this solution will be required. Then dilute to 100 ml.

5) Dithizone reagent . . . . 100 mg/l

Dissolve 100 mg. of pure dithizone in 50 ml. of zinc-free CCl_4, and filter to remove any solids. Run the

---

- Available from J.T. Baker Chemical Co., Phillipsburg, N.J.

filtrate into a separatory funnel and shake with 50 ml. of 1% NH_4OH. Run the CCl_4 layer into another separatory funnel and shake with 50 ml. more 1% NH_4OH. Then discard the CCl_4 layer and combine the orange colored aqueous extracts. Wash the aqueous solution with 10 ml. portions of CCl_4 three times and then acidify with 2 ml. of concentrated HCl precipitating the dithizone. Finally, extract the dithizone with 10 ml. portions of CCl_4 until the aqueous layer becomes colorless, and dilute the combined extracts to a liter with CCl_4. Cover the green dithizone solution with a 1/2 inch layer of 5% aqueous hydroxylamine hydrochloride to retard oxidation. The solution should be kept in a pyrex flask, and stored in a cool, dark place.

6) Standard zinc solution . . . . . . 1.0 micrograms/ml.

Dissolve 100 mg. of pure zinc in 10 ml. of 1-1 HCl and dilute to 1 liter. One ml. of this stock solution is diluted to 100 ml. to obtain a solution containing one microgram of zinc per ml.

7) Distilled water . . . . zinc-free

Water should be tested for zinc by adding 5 ml. of dithizone to 25 ml. of H_2O made alkaline with a drop of NH_4OH. On shaking, the CCl_4 layer should be colorless or very weakly pink, showing no or little zinc present. Water obtained from a pyrex glass or a block tin still was found to be pure.

8) Carbon tetrachloride . . . . zinc-free

All CCl_4 used should first be distilled in a pyrex still at least once, and preferably twice, to insure zinc-free carbon tetrachloride.

9) Wash solution . . . . 0.35 NH_4OH

Add 3.5 ml. of concentrated NH_4OH to zinc-free distilled water to make a liter of solution.

Apparatus Required:

1) Colorimeter or spectrophotometer -- A Klett-Summerson colorimeter with a green #54 filter was used with a testtube cell 0.5 inches in diameter. Any other colorimeter or spectrophotometer may be used.

2) Volumetric flask - 50 ml.

3) Pipettes

4) Separatory funnels - 60 to 125 ml. Squibb type funnels

5) Burettes

6) Long stem funnel and qualitative filter paper.

Procedure:

Extraction of Copper and Iron

1) From a 1 ml. pipette graduated in tenths, pipette a .1 ml. sample of the nickel bath to be analyzed, into a 60 ml. separatory funnel. One can also dilute 10 ml. of the bath to 100 ml. with distilled water and take 1 ml. for analysis.

2) Add 25 ml. of zinc-free distilled water.

3) From a dropping bottle, add about 20 drops of 1% cupferron. Shake about 30 seconds.

4) Add 10 ml. of amyl acetate, shake for a few times, and allow the aqueous layer to settle. Run the aqueous layer into a clean separatory funnel, discarding the amyl acetate extract.

5) Repeat the extraction with another 10 ml. portion of amyl acetate, discarding the amyl acetate after running the aqueous layer into a clean separatory funnel.

Formation of Heavy Metal Complexes

6) Add 2 ml. of 10% sodium tartrate.

7) Run in, from a burette, 10 ml. of the carbamate reagent.

8) Add 25 ml. of distilled zinc-free water and shake for about 2 minutes. The color of the solution changes from dark brown to yellow, and a green precipitate forms at this point. This is the nickel complex.

Formation of the Colored System

9) Run in from a burette 5 ml. of dithizone reagent.

10) Shake vigorously for one minute. Allow the carbon tetrachloride layer to settle, and then run the lower layer into another separatory funnel. Allow the carbon tetrachloride to drain out even though some of the green precipitate goes with it.

11) Repeat steps (9) and (10) until the carbon tetrachloride layer comes through with a greenish or colorless tint, indicating that all the zinc has been extracted from the aqueous solution which is discarded.

12) The carbon tetrachloride solution may now be freed of any entrained precipitate by washing with 25 ml. of zinc-free distilled water. After shaking and allowing the organic layer to settle, run it into another clean separatory funnel.

13) Now add 15 ml. zinc-free water and 5 ml. of the carbamate reagent. Shake for 30 seconds. The greenish color of the excess dithizone should disappear, leaving a pure red or pink color. If all the excess dithizone is not removed, the carbon tetrachloride layer is run into another separatory funnel, and washed again with 15 ml. of dilute ammonium hydroxide wash solution.

14) Carefully run the red solution into a 50 ml. volumetric flask, and dilute to the mark with zinc free carbon tetrachloride.

15) Filter to remove any water present, and collect the filtrate in a clean dry beaker.

Measurement of Extinction

16) Using a testtube cell, with carbon tetrachloride as the reference liquid, zero the colorimeter by adjusting the galvanometer to the zero position with the scale reading at zero. If a spectrophotometer is used, set the wave length dial at 535 millimicrons before adjusting to zero.

17) Replace the reference liquid with the red zinc dithizonate-carbon tetrachloride solution.

18) Take 5 readings and record the average as the colorimeter reading for the sample.

19) Run a blank, following exactly the same procedure except that no sample is taken.

Calculations

The colorimeter reading obtained for the blank is deducted from that obtained for the sample. This is the corrected reading and is referred to the calibration curve to determine the quantity of zinc present in the 0.1 ml. sample of nickel plating bath. This method of correction for the blank is applicable only when the colorimeter scale is in extinction units or in units proportional to extinction.

If the colorimeter reading obtained for a sample is, for example, 153 and the blank 30, the corrected reading would be 153 - 30, or 123. From the calibration curve, a reading of 123 corresponds to 10 micrograms of zinc. Therefore, the nickel bath tested contains 100 micrograms per milliliter, or 100 ppm.

Since the calibration curve is a straight line, the amount of zinc present may be calculated without resort to the calibration curve. The unknown nickel bath, a bath with a known amount of zinc, and a blank, are run according to the regular procedure. The following equation yields direct results:

$$\frac{\text{Ppm Zinc in known sample}}{\text{Corrected colorimeter reading of known}} \times \text{Corrected Reading of unknown Sample} = \text{ppm zinc in unknown}$$

Accuracy and Precision Obtained

Table III shows the results obtained when a 50-50 nickel plating bath was analyzed according to the procedure described. The bath contained "impurities", as previously described and listed in Table I. The accuracy does not in general exceed 10% and the precision is of about the same order of magnitude.

Table III

Micrograms Zinc added	Colorimeter Readings	Blank Readings	Corrected Readings	Micrograms Zinc Obtained	Error	% Error
2	57	30	27	2.2	+ .2	10
	81	56	25	0.0	0.0	0
5	89	30	59	4.75	-2.5	5
	118	56	62	5.0	0.0	0
10	151	32	119	9.5	-0.5	5
	186	56	130	10.4	+0.4	4
	186	69	117	9.4	-0.6	6
	181	69	112	9.0	-1.0	10
	205	90	115	9.2	-0.8	8
	184	58	126	10.1	+0.1	1
	196	70	126	10.1	+0.1	1
	194	70	124	10.0	0.0	0
15	244	58	186	15.0	0.0	0
20	374	120	254	20.4	+0.4	2
	400	120	280	22.5	+2.5	12.5

In order to further check the method for accuracy and duplicability, the following commercial laboratories kindly consented to run analyses on a synthetic test bath according to the procedure described in this paper. The authors wish to express their thanks for this cooperation. The companies are: International Nickel Company, Bureau of Standards, Bethlehem Steel Corporation, Rock Island Arsenal, and Lehigh University.

"Stop and Go" Method

The following procedure may be used in the estimation of zinc traces in nickel plating baths without the use of a colorimeter.

Procedure:

1) Follow the same procedure as that described under "Routine Procedure" through step (8).

2) Using 2 ml. portions of dithizone reagent, extract the zinc as in the "Routine Procedure" and drain off the red carbon tetrachloride layer after each extraction.

3) When the carbon tetrachloride layer remains green after shaking one minute, record the total volume of dithizone required to extract all the zinc.

4) Compare the amount of dithizone taken for an unknown with the amount required for several known solutions run in the same manner.

Results:

A pure 50-50 nickel plating bath was run according to the described procedure with added quantities of standard zinc solution. The results are shown in Table IV.

Table IV

"Stop and Go" Results

Micrograms of Zinc added	No. of Extractions Required	Total volume of Dithizone Required
5	3	6 ml.
10	4	8
20	6	12

The nickel bath sent out was the 50-50 bath of the same composition as that described in this paper, and contained the same impurities as listed in Table I. The zinc concentration was 100 micrograms/ml. of bath.

Table V

Check Analyses Results

Laboratory	Ppm Zn Added	Ppm Zn Found
A		
B		
C		
D		
E		

Applicability of Method

Any nickel plating bath may be analysed satisfactorily by the described procedure. The only interfering ions not included in the tests were silver and mercury, which are usually not present in a nickel plating bath. The method was also found to give satisfactory results with Watts type, all chloride, and high sulfate baths.

SPECIAL PRECAUTIONS

All reagents must be zinc-free, or nearly so, in order to obtain a low blank. All glassware must be kept clean, and should be thoroughly rinsed with zinc-free distilled water before use. Separatory funnels should be *kept stoppered* to prevent possible contamination during a run, and burette should be *kept covered at all times*.

Water may be freed of zinc by distilling in pyrex equipment. Water used for this investigation was taken directly from a large laboratory still with a block tin condenser, and proved to be of satisfactory purity. All the carbon tetrachloride used was distilled twice in pyrex equipment.

Summary

A colorimetric method for the determination of traces of zinc in nickel plating baths has been developed using dithizone. Copper and iron are first removed by the formation of their cupferrides and their extraction with amyl acetate. Heavy metal impurities including nickel are then complexed with sodium di(β-hydroxyethyl)dithiocarbamate, referred to in this paper as "carbamate reagent". Zinc dithizonate is formed in the presence of these complexes, using a carbon tetrachloride solution of dithizone. After removing the excess dithizone, the zinc is determined colorimetrically by measuring the amount of incident light absorbed by the red zinc dithizonate in a colorimeter, using a green filter. A "Stop and Go" method which may be used in the estimation of zinc is described. It cannot be repeated too often that all apparatus and all the reagents used must be absolutely free of zinc. Otherwise high blanks and erratic results will be obtained.

FIGURE (1)

Micrograms of zinc as zinc dithizonate, in 50 ml. total volume of carbon tetrachloride are plotted against corrected colorimeter readings.

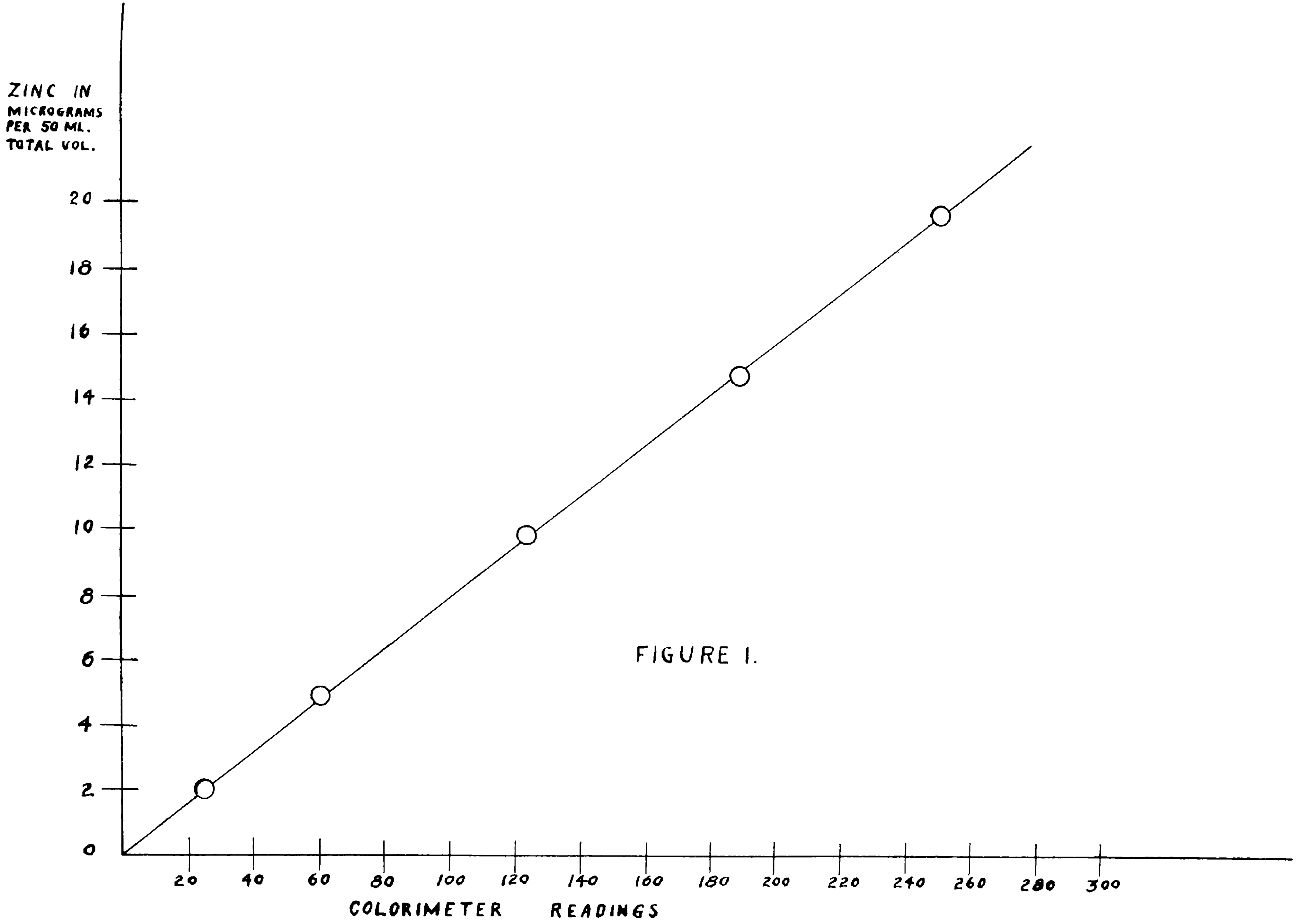

ZINC IN MICROGRAMS PER 50 ML. TOTAL VOL.
20
18
16
14
12
10
8
6
4
2
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300
COLORIMETER READINGS

FIGURE I.

FIGURE (2)

Curve (a) -- Extinction is plotted against wave length in millimicrons, for 5 micrograms of zinc dithizonate in 25 ml. of carbon tetrachloride.

Curve (b) -- Extinction is plotted against wave length for the green #54 filter. Extinction values at right apply to curve (b).

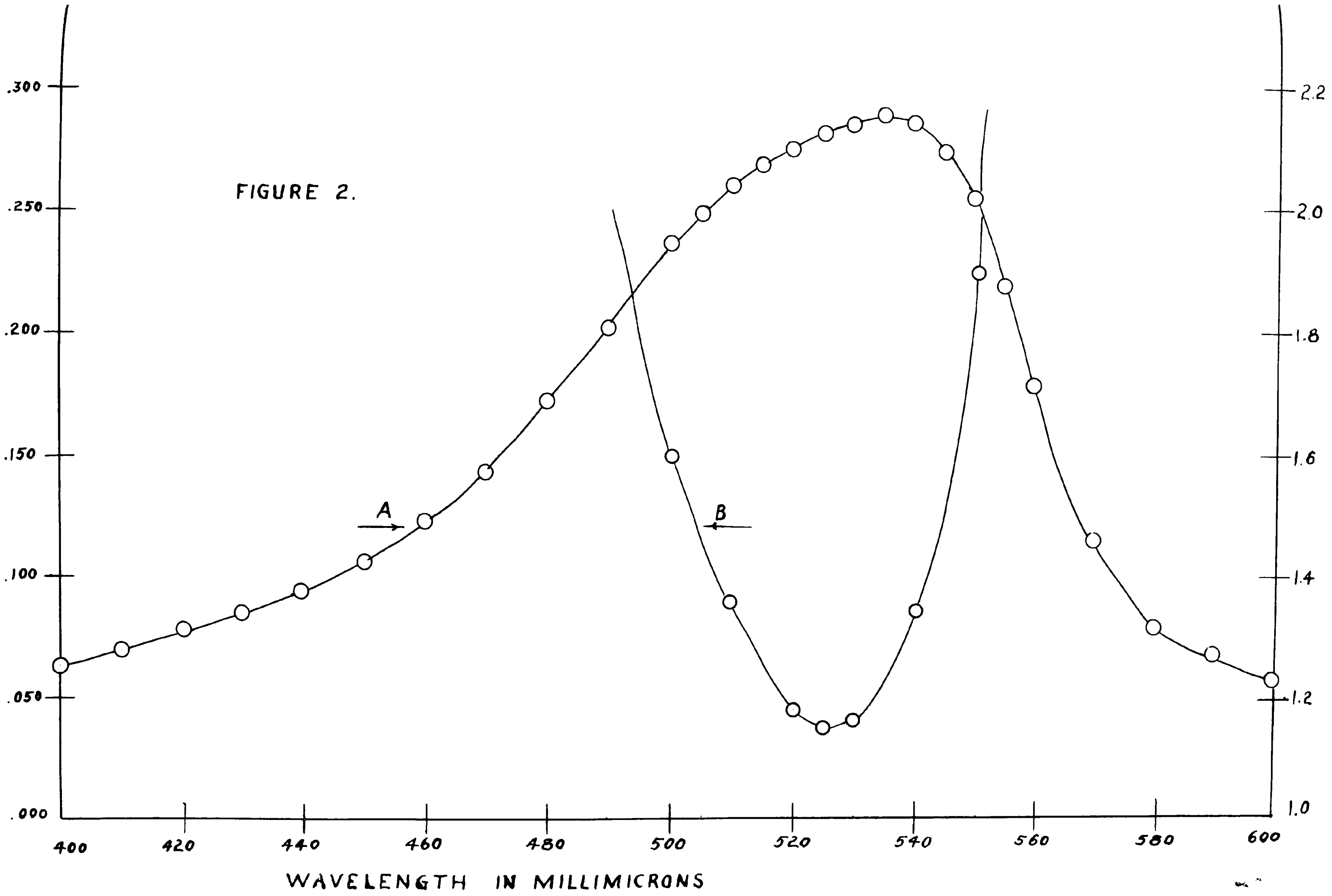


FIGURE 2.

.300
.250
.200
.150
.100
.050
.000
2.2
2.0
1.8
1.6
1.4
1.2
1.0
400
420
440
460
480
500
520
540
560
580
600
WAVELENGTH IN MILLIMICRONS
A
B

SECTION H

THE DETERMINATION OF ALUMINUM IN NICKEL PLATING BATHS

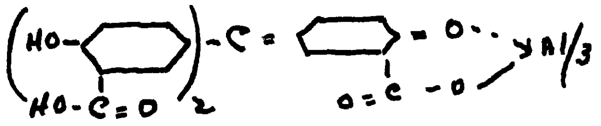
DETERMINATION OF TRACES OF ALUMINUM IN NICKEL PLATING BATHS

This investigation was conducted for the purpose of obtaining a rapid, accurate method for the determination of traces of aluminum as an impurity in nickel plating baths. Other ions present in the nickel plating solutions as impurities were cadmium, copper, lead, manganese, iron, zinc, calcium, silicate and chromate ions. The method thus had to be applicable to solutions containing large concentrations of nickel as well as appreciable quantities of other interfering elements.

Various methods for the quantitative determination of aluminum may be found in the literature. These range from gravimetric through colorimetric methods as well as spectrographic. Since very small quantities of aluminum could not be determined by such methods as that of Willard and Tang (131), who determined aluminum by precipitation with urea, or the method of Cunningham (25), who determined aluminum in ferrochrome and chromium metal by precipitation of $Al(OH)_3$, these methods were not studied further. Spectrographic methods such as that of Tourtellotte (125), who studied biological materials, were not pursued since the high cost of equipment made the methods impractical for the purpose desired. Colorimetric methods had been successfully employed in determining aluminum in water, biological materials, etc., therefore, it was decided to attempt to adapt some known method to the needs stated here.

The colorimetric determination of aluminum is based upon the formation of strongly colored lakes with a suitable organic reagent. The exact nature of the lakes are not definitely known, but may be regarded as colloidal aluminum hydroxide upon which the organic reagent, or dye, is adsorbed, producing a strong color. The intensity of the color is dependent on the concentration of aluminum. Some of the reagents in common use for colorimetric methods are ammonium aurintricarboxylate, sodium alizerin sulfonate, eriochromcyanin and hematoxin (51, 68). Of these, ammonium aurintricarboxylate (hereafter referred to as "aluminon" in this paper) is in wide use in the United States (28, 76, 86, 93, 111, 134, 136). Since aluminon is available in a pure form, and appeared to give results as satisfactory as the other colorimetric methods, it was decided to try to apply this method to nickel plating baths.

Although aluminum may be determined in basic medium by the aluminon method (111), the method has been found to give reproducible results on the acid side, with greater simplicity of operation (110). Therefore, it was decided to use the direct method, by which the red color developed in acid medium is measured or compared. The red color formed has been ascribed to an internal complex salt with the following structural formula, by Fiegl:



Developmental Work

Since nickel, iron, and other metallic ions present in nickel plating baths interfere with the aluminon method as well as all other colorimetric methods, a method of removal was the first problem in developing a working procedure. If the large amount of nickel were precipitated and filtered off, it was felt that a large loss of aluminum would occur, through adsorption and entrapment. Electrolysis with a mercury cathode in dilute sulfuric acid solution has been used to eliminate all interfering metals at one stroke (110). However, the procedure is quite lengthy. Hence, it was decided to attempt to precipitate the nickel with some organic reagent, and remove this from the aqueous solution by extracting with an organic solvent. Sodium diethyl dithiocarbamate was found to be suitable for precipitating the nickel, and it was found possible to extract this precipitate with chloroform. About 90 milligrams of nickel can be removed in this manner with about 35 ml. of chloroform by this method.

Tests were also made using dimethylglyoxime to precipitate the nickel. However, after trying chloroform, carbon tetrachloride, n- and iso-amyl alcohol, n-butyl alcohol, benzene, and ether as solvents, all unsuccessfully, this reagent was abandoned. Similar tests were made using diethanol dithiocarbamate and the same solvents. These tests were also unsuccessful.

To remove iron which interferes badly with the aluminon method, a 1% solution of cupferron was used since this method has been widely used to remove small amounts of iron from aqueous solutions (7, 8, 75). Amyl acetate readily dissolves the iron cupferride, and one or two extractions were found sufficient to remove all the iron from an "impure" nickel plating bath (50-50 bath) containing .001 gram of iron per ml. One ml. of 1% cupferron was used.

After having removed all the nickel and any iron from the sample the determination of the aluminum was quite simple. A procedure was worked out closely following that given by Sandell (110), with a few modifications which are described in the Recommended Routine Procedure.

In extracting the nickel by this method the pH of the nickel bath must be adjusted to about 2.0 and kept at this pH. If it is much higher, some aluminum may be extracted with the nickel. If it is too high, appreciable quantities of the diethyldithiocarbamate will be decomposed. It was found that one ml. of (1:1) hydrochloric acid added to one ml. of the bath was enough to keep the pH at about 2.0 while the nickel was extracted. In tests on the synthetic "impure" bath described below, 5 ml. of the diethyldithiocarbamate solution was added after the first extraction of nickel to be certain of complexing any remaining nickel. This necessitated a further addition of HCl to bring the pH down to about 2.0. Thus, by making the addition of 1-1 HCl in two separate portions, the dual purpose of removing the interfering ions as well as keeping all the aluminum in the aqueous solution is accomplished.

Adding all the acid at once would prevent complete removal of the nickel by destroying much of the carbamate reagent before it could combine with the metallic ions. This, in fact, was tried with unsatisfactory results.

Preparation of Calibration Curve

After obtaining satisfactory results in extracting the nickel and other interfering ions using cupferron and diethyldithiocarbamate, a calibration curve was prepared using a pure synthetic 50-50 bath. This consisted of a 3 N nickel solution composed of 1.5 N nickel sulfate plus 1.5 N nickel chloride, with 30 gr. of boric acid per liter.

To 1 ml. portions of the 50-50 bath were added varying quantities of standard aluminum solution. The Recommended Routine Procedure described in the latter portion of this paper was then followed with the exception of steps (3), (4), and (7). The data obtained is recorded in Table I. By plotting the average values obtained for each quantity of aluminum taken, the curve in Figure 1 was obtained. A Klett-Summerson photoelectric colorimeter with the green # 54 filter was used in making all determinations. This filter transmits the greatest amount of light at 525 millimicrons, which is the range at which the aluminum-ammonium aurintricarboxylate (aluminon) colored.system shows the highest absorption.

Figure 2 shows the transmittancy curves for both the # 54 filter and the colored system obtained with a Beckman ultraviolet spectrophotometer.

Table I

Calibration Curve Data

Aluminum Added Micrograms	Readings	Blank	Corrected Readings	Average
10	109	67	42	40
10	117	77	40	
10	116	77	39	
20	154	85	69	66
20	151	85	66	
20	144	80	64	
40	185	80	105	108
40	178	67	111	
40	174	67	107	
50	186	65	121	123
50	184	67	117	
50	198	67	131	
50	206	85	121	
60	219	80	159	144
60	216	67	149	
60	215	67	148	
60	208	67	141	
70	236	77	159	160
70	241	80	161	
70	241	80	161	

Accuracy and Precision

The method was finally checked for accuracy and precision by running several determinations on a 50-50 nickel bath to which various ions had been added as "impurities". Table II lists the amount of each metal added. These metallic ions were added wherever possible as solid chlorides, sulfates, or nitrates, and the solution filtered to remove any undissolved matter.

Table II

Ions Added to Nickel Plating Bath as Impurities

Ion Added	Quantity in g/1	Added As
Cadmium	0.2	$CdCl_2 \cdot 2\ 1/2\ H_2O$
Chromium	0.2	CrO_3
Copper	1.0	$CuCl_2 \cdot 2H_2O$
Lead	0.05	$Pb(C_2H_3O_2)_2 \cdot 3H_2O$
Manganese	1.0	$MnCl_2 \cdot 4H_2O$
Iron	1.0	$FeCl_3 \cdot 6H_2O$
Silicon	1.0	Na_2SiO_3
Zinc	1.0	$ZnSO_4 \cdot 7H_2O$
Calcium	(saturated)	$CaBr_2$

All results are shown in Table III from which it may be seen that the average error obtained for all tests was about 5.5%, with the greatest error at about 8.5%. The precision shown is probably satisfactory for routine control work.

Table III

Accuracy and Precision Data

Al Added Micrograms	Readings	Blank	Corrected Readings	Al Found	% Error
20	141	72	69	21	+ 5%
40	168	67	101	38	- 5
50	193	67	126	51	+ 2
50	199	67	132	54	+ 8
50	193	67	126	51	+ 2
50	198	67	131	53	+ 6
50	195	67	128	52	+ 4
60	203	67	136	56	- 6.6
70	217	67	150	64	- 8.5

To further check the method for accuracy, samples of a nickel bath (50-50) with 50 micrograms of aluminum present were sent to several commercial laboratories for analysis. Copies of the method were included and the following organizations kindly cooperated in testing the method:

The results obtained from these laboratories are shown in Table IV.

Table IV

Check Analysis Results

Recommended Routine Procedure

The procedure adopted for the colorimetric determination of aluminum in nickel plating baths is the following:

Reagents Required:

1) Aluminon solution 0.5%

Dissolve 0.5 gm. of aluminon (ammonium aurintricarboxylate) in 100 ml. distilled water. Make up fresh solution every two to three days.

2) Cupferron solution 1%

Dissolve .25 gm. cupferron in 25 ml. distilled water. Keep the solution cool and make up fresh solution every day.

3) Chloroform . . . . reagent grade

The chloroform should be free of aluminum.

4) Amyl acetate . . . . c.p. grade

5) Hydrochloric acid . . . . (1:1)

Dilute c.p. grade concentrated hydrochloric acid with an equal value of distilled water.

6) Hydrochloric acid . . . . (1:9)

Dilute 10 ml. of c.p. grade concentrated hydrochloric acid with 90 ml. of distilled water.

7) Ammonium hydroxide . . . . (1:9)

Add 10 ml. of c.p. grade concentrated ammonium hydroxide to 90 ml. of distilled water.

8) Diethyl dithiocarbamate (Na salt) 10%

Dissolve 100 grams of the salt in 800 ml. of aluminum free distilled water and dilute to a liter. Filter off any undissolved matter.

9) Ammonium acetate buffer solution 10%

Dissolve 100 gms. ammonium acetate, c.p. grade, in distilled water to make 1 liter of solution.

10) Standard aluminum solution . . . . 10 micrograms/ml.

Dissolve 0.1 gram of pure metallic aluminum in 20 ml. of concentrated HCl and dilute to a liter. Dilute 10 ml. of this stock solution to 100 ml.

Apparatus Required:

1) Volumetric flasks - 100 ml. volume

2) Separatory funnels - Squibb type, short-stemmed funnels of 100-125 ml. capacity.

3) Pipettes and burettes

4) pH meter of its equivalent

5) Colorimeter or spectrophotometer -- A Klett-Summerson colorimeter with a green #54 filter was used, with a testtube cell. Any colorimeter or spectrophotometer may be used.

Procedure:

Separation of Interfering Metals

1) Pipette a 1 ml. sample of the nickel plating bath into a separatory funnel.

2) Add 1 ml. of (1-1) HCl and 25 ml. of distilled water.

3) Add 1 ml. of 1% cupferron and shake for one minute.

4) Add 10 ml. of amyl acetate, shake for one minute, let the aqueous layer settle and run it into a clean separatory funnel. Repeat this with 5 ml. of amyl acetate.

5) Run 10 ml. of 10% carbamate solution into the aqueous solution and shake for 2 minutes, being careful to release the pressure built up by the gas formed in the reaction.

6) Add 25 ml. of chloroform and shake for 2 minutes. Draw off the chloroform (bottom) layer as soon as settling is complete.

7) Add 5 ml. more of 10% carbamate, and shake for one minute; then add 1 ml. of 1-1 HCl and shake again for one minute.

8) Extract with 5 ml. portions of chloroform until the chloroform comes through completely colorless. This usually requires 3 to 4 extractions.

9) Run the clear aqueous solution through a qualitative filter, catching the filtrate in a 150 ml. beaker. Wash the paper about five times with distilled water.

Development of the Colored System

10) Make the aqueous solution neutral with (1-10) NH_4OH using a pH meter or other means. The volume should not be nearly 75 ml.

11) Add 1 ml. of (1-9) HCl, and stir the solution to assure uniform mixing. Make the volume up to 75 ml.

12) Pipette 1 ml. of 0.5% aluminon dye into the beaker and mix.

13) Add 10 ml. of 10% ammonium acetate buffer, and dilute to 100 ml. in a volumetric flask and mix well. Record the time.

Measurement of Solution Transmittancy

14) Partially fill the testtube cell with water as the reference liquid and adjust the galvanometer needle to zero when the dial reading is zero. If the instrument used has a wave length selector, set it at about 540 millimicrons.

15) Rinse out the testtube a few times with small portions of the red aluminum lake, replace the testtube in the instrument and rotate the dial until the galvanometer needle is once again at its zero position. Record the reading on the scale attached to the dial.

16) Run a blank in a similar manner except that a sample of the bath is omitted.

17) Subtract the blank reading from the sample reading to get a corrected measure of the amount of light transmitted by the sample. If the scale reading gives the extinction of the sample directly or is related to the extinction.

18) Look up the corrected scale reading of the sample on the calibration curve and the quantity of aluminum corresponding to this reading is the amount present in one ml. of the bath.

Calculations

If the reading obtained with the unknown is 172 and that of the blank is 67; the corrected reading of the unknown is 105. According to the calibration curve, this reading corresponds to 40 micrograms of aluminum. Since a one ml. sample was taken for analysis, the bath contains 40 micrograms of aluminum per milliliter or 40 ppm.

"Stop and Go" Method

If a colorimeter is not available, the amount of aluminum present in nickel plating baths may be estimated according to the following procedure:

1) Follow "Routine Procedure" through step (13).

2) Prepare a series of standards, using 0, 20, 40, 60, and 80 micrograms of aluminum in pure nickel bath, using the same procedure as in the preparation of the calibration curve.

3) Having added the aluminon dye and the ammonium acetate buffer to all the standards as well as the unknown, at about the same time, compare the unknown to the series of standards after 1/2 hour, by viewing the solutions in Nessler tubes horizontally against a white background. The amount of aluminum in the unknown is approximately equal to the amount of aluminum in the standard solution whose color it most nearly matches.

By this method one may estimate the amount of aluminum present in one ml. of nickel plating bath within 20 micrograms.

Discussion

In applying this method there are several factors that must be carefully controlled:

1) The pH of the solution must be acid enough to prevent the loss of aluminum when the nickel is precipitated with the

diethyldithiocarbamate. When the pH is around 3.5 or so, results were erratic while when the solution was quite acid, some sulfur and CS_2 were formed as a result of the decomposition of the reagent. At a pH around 2.0, there is no apparent loss of aluminum and little decomposition of the reagent.

2) The purpose of the filtration is to remove material that will cause the red aluminum lake to be cloudy in appearance if it is not removed. Tests showed that there is no appreciable loss of aluminum when the aqueous solution remaining after the chloroform extractions are filtered.

3) Due to the solutions possibly having different acidities after the chloroform extractions, it is necessary to adjust the pH to about 7.0 and then add the amount of hydrochloric acid recommended so that all solutions will have the same pH when the aluminon reagent and the buffer is added. The additions must be made in the order given if consistent results are to be obtained. Aluminon must not be added when the solution is neutral or slightly basic as the results become quite erratic. The total volume of the solution before the addition of the aluminon reagent should also be about the same at all times--around 75 ml.

4) The color of the aluminon lake does not develop immediately to its maximum. In fact, after a half hour, the maximum is not reached, but the rate of change has become so slow that for the purposes of getting a reading it is no longer changing in intensity.

Summary

A method for the determination of aluminum in nickel plating baths is proposed using the standard aluminon dye colorimetric procedure, after removal of interfering metals. Iron is first removed by the extraction of iron cupferride with amyl acetate. The large amount of nickel present is removed by complexing it with sodium diethyldithiocarbamate, followed by extraction with chloroform. The color of the aluminon lake is developed by adding aluminon and a buffer to adjust the pH to 5.5. After standing 30 minutes, the transmittancy of the lake is measured with a Klett-Summerson colorimeter using the # 54 green filter which may be purchased with the instrument.

FIGURE (1)

Calibration curve for the determination of aluminum in a 50-50 type nickel plating bath by the aluminon method using a Klett-Summerson colorimeter with green #54 filter.

Cell -- testtube of approximately 12 mm. internal diameter.

Final Volume of Solution -- 100 ml.

FIGURE I.

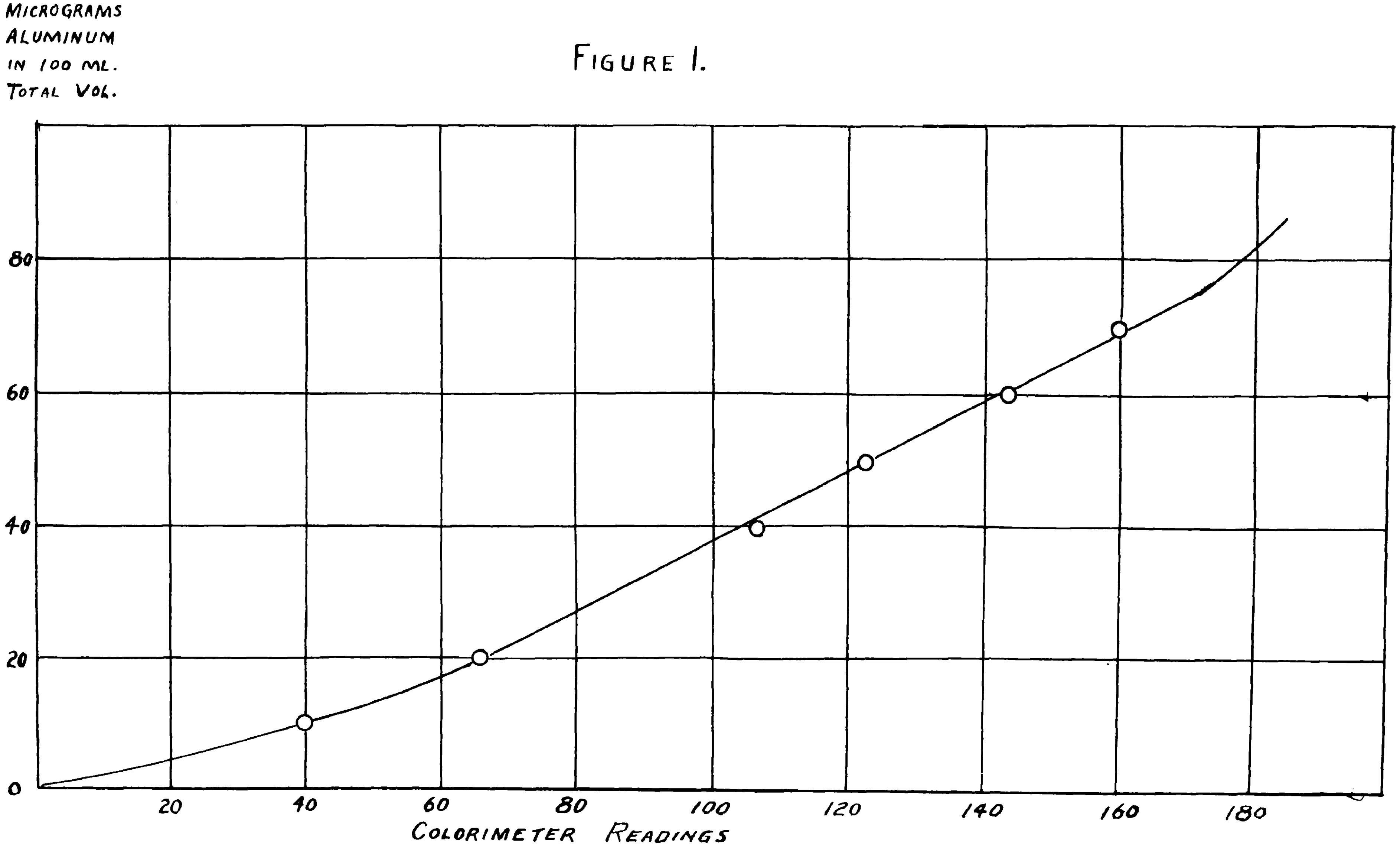

MICROGRAMS
ALUMINUM
IN 100 ML.
TOTAL VOL.
80
60
40
20
0
20
40
60
80
100
120
140
160
180
COLORIMETER READINGS

FIGURE (2)

Curve (a) -- Extinction versus wave length for the red aluminum lake with aluminon with 80 micrograms of aluminum in a final volume of 100 ml. Thickness of cell was 1.00 cm.

Curve (b) -- Extinction versus wave length for the Klett-Summerson green #54 filter. The extinction units on the right apply to this curve.

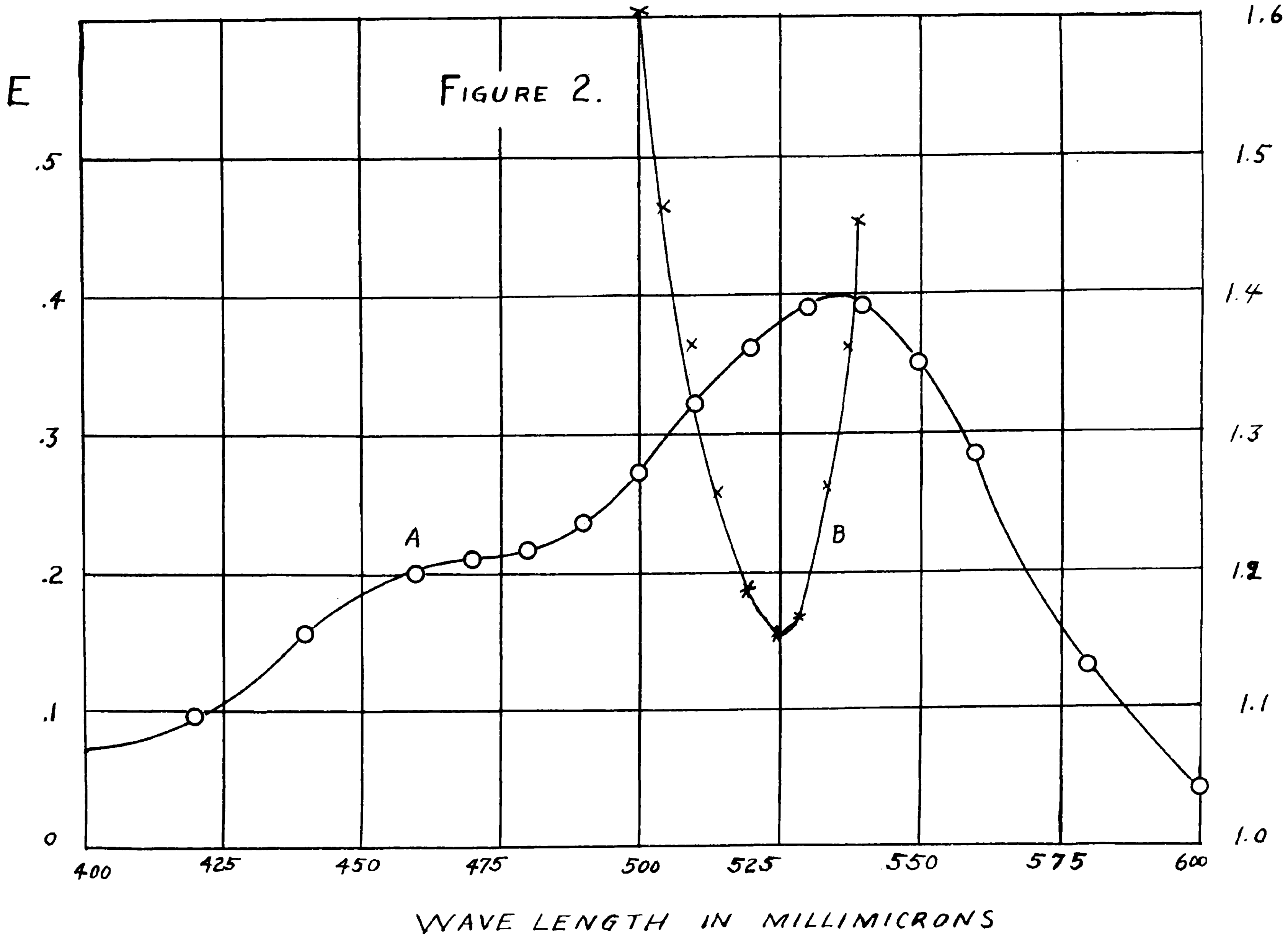


FIGURE 2.

E
.5
.4
.3
.2
.1
0
1.6
E
1.5
1.4
1.3
1.2
1.1
1.0
A
B
400
425
450
475
500
525
550
575
600
WAVE LENGTH IN MILLIMICRONS

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